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Pure green chemical approach for synthesis of Ag₂O nanoparticles

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ABSTRACT

In this study, a green chemistry method is reported for the synthesis of Ag₂O nanoparticles with the utilization of starch molecules as a stabilizing agent. In particular, by simply adjusting the concentration of starch in the reaction media, the structure of Ag₂O nanoparticles can be engineered in disc and faceted shapes, which has been analyzed by transmission electron microscopy, UV-Vis spectroscopy, and X-ray diffraction technique. In addition, antibacterial activity of the prepared Ag₂O nanoparticles had been evaluated against food poisoning and pathogenic bacteria.

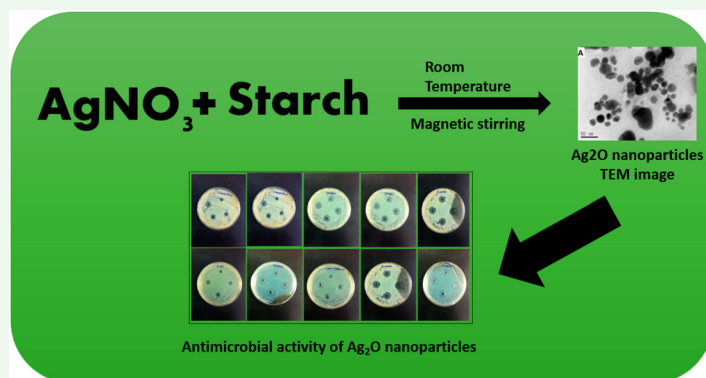
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Nanoparticle; disc shape; green chemistry; Ag₂O



1. Introduction

The generation of nanomaterials is a major milestone in technological development. The chemical synthetic methods generate new materials for sensing, plasmonics, sophisticated drug delivery system in medicine, and energy-efficient components in electronics and computing. The products based on nanotechnology are currently on the market of which majority are incorporated in everyday personal-care products, cosmetics, and clothing (1). The demand for such nano-based products will be increasing. And environmental impacts of such chemical synthetic processes will be severe.

Ag₂O is a p-type semiconductor with a band gap of 1.46 eV. It has been extensively used in the production of ethylene oxide as a catalyst and used as a co-catalyst in palladium-catalyzed reactions in organic synthesis (2). Lu et al. developed a simple method for colorimetric

detection of sulfite developed on the basis of the finding that the oxidase-like activity of Ag₂O nanoparticle was inhibited by sulfite (3). Yang et al. showed that Ag₂O is more efficient than Ag colloid and many other metal oxides for the photocatalytic degradation of methylene blue in solution when utilizing visible light (4). The different crystal structures of Ag₂O offer a variety of interesting physicochemical properties, such as the catalytic, electrochemical, electronic, and optical properties (5).

Ag₂O powder has been prepared for over 100 years by mixing silver nitrate and barium hydroxide solutions (6, 7). Over the past decade, a variety of techniques have been employed for the synthesis of Ag₂O with different morphologies. For example, the Ag₂O hexapod was prepared by making silver ions (Ag⁺) react with hydroxide ions in the presence of ammonia, pyridine, or bis-(p-sulfonatophenyl) – phenylphosphine

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dihydrate dipotassium – to control the morphological shapes (8–11). A lot of electrochemical synthesis methods offered Ag_2O particles in different shapes in micro and nanosizes (12, 13). In these chemical syntheses, a hazardous chemical and an organic solvent were used for the control of particle size and shape, which are hazardous to the environment.

Therefore, researchers had started using biological molecules as a template for synthesizing nanomaterials. Raveendran et al. reported the use of starch as a stabilizer in the generation of Ag nanoparticles. They used β -D-glucose as the reducing agent, and the synthesis was completed within 1 h. Starch can be easily dispersed in water, so the use of organic solvents can be avoided (14). Starch consists of two types of molecules, namely linear or helical amylose and branched amylopectin. It is recognized as the second most abundant biopolymer in nature and also biodegradable, non-toxic and low-cost production; hence, used as a raw material in different industries (15–17).

To the best of our knowledge, the use of a non-toxic reactant such as starch, for generating Ag_2O nanostructures, has not yet been reported to date. Raveendran et al. prepared Ag nanoparticles using starch and glucose, but in the present study Ag_2O nanoparticles were prepared without using glucose. Ag_2O nanoparticles are used as a catalyst, and the nano size range will

definitely increase the catalytic activity. In the present study, the Ag_2O nanoparticles were synthesized simply at room temperature with starch as the stabilizer, that is the complete green synthesis is employed and obtained Ag_2O nanoparticles are of the size of below 100 nm. Synthesized nanoparticles were characterized by UV-Vis spectrophotometry, transmission electron microscopy (TEM), and further confirmed by the X-ray diffraction (XRD) technique. The antibacterial activity was evaluated on food poisoning and pathogenic Gram-positive (*Bacillus cereus*, *Staphylococcus aureus*, *Staphylococcus saprophyticus*, *Listeria monocytogenes*) and Gram-negative bacteria (*Escherichia coli*, *Proteus vulgaris*, *Pseudomonas putida*, and *Salmonella typhi*).

2. Experimental procedure

2.1. Materials and methods

All reagents were of analytical grade and used without further purification. In a typical synthesis, 20.4 mg of soluble starch (Junsei chemicals) was dissolved in 8 ml of deionized (DI) water in a 20 ml vial. Meanwhile, 3 ml of an aqueous solution containing AgNO_3 (20 mM), that is 10 mg, was rapidly added into the vial. To dissolve starch the solution was vortexed for 5 min. After the vial had been capped, the reaction mixing was continued at

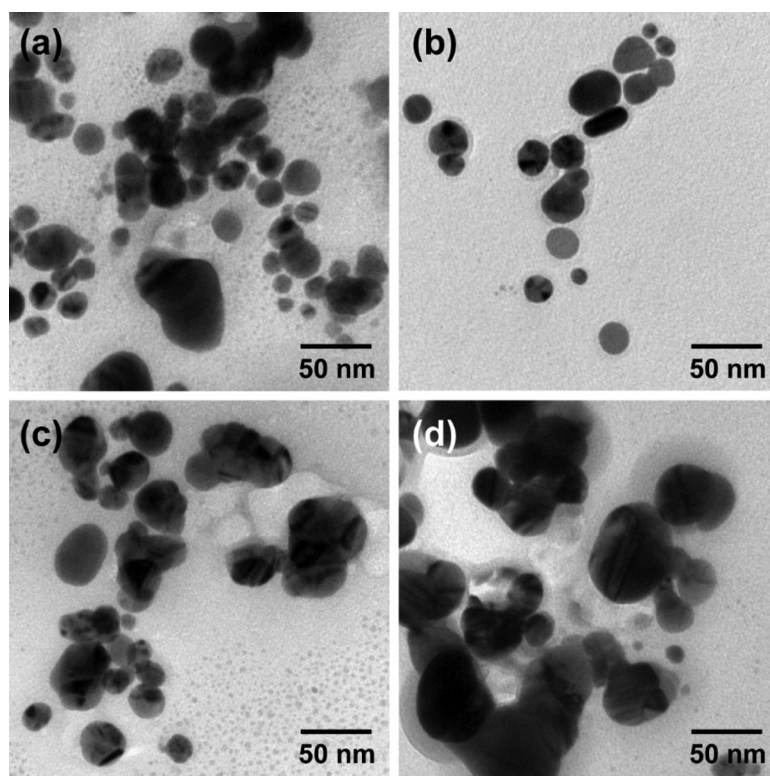


Figure 1. TEM images of Ag_2O nanoparticles prepared with different weight ratios of starch to AgNO_3 : (a) 1.5, (b) 2, (c) 5, and (d) 10.

room temperature in air with a magnetic stirrer for 24 h. The different reactions were carried out by varying the concentration of AgNO_3 and starch in other sets of reactions. The weight ratio of starch to AgNO_3 was changed for different sets as 1.5, 2, 5, and 10. The final product was collected by centrifugation and washed three times with hot DI water to remove most of the starch. During the washing process, the suspension was centrifuged at 13,800 rpm for 12 min. Finally, the precipitate was re-dispersed in DI water for further use.

2.2. Characterizations

The TEM sample was prepared by placing a drop of the final product on a carbon-coated copper grid, and then

was dried by hot air. The final sample has been stored in a copper grid case. The TEM imaging was performed using a Hitachi H-7500 microscope operating at 120 kV. The UV-Vis-NIR spectra were recorded using a spectrophotometer Jasco V-650. The XRD was performed on the instrument Philips X'pert-MPD-system with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The crystalline size of Ag_2O nanoparticles was calculated using Debye-Scherrer's equation as follows:

$$D = \frac{K\lambda}{\beta \cos \theta},$$

where K is the Scherrer's constant ($K = 0.94$), D is the mean crystalline size, λ is the X-ray wavelength (0.1546 nm), β is the full-width at half-maximum of the XRD line in radians, and θ is the half diffraction angle.

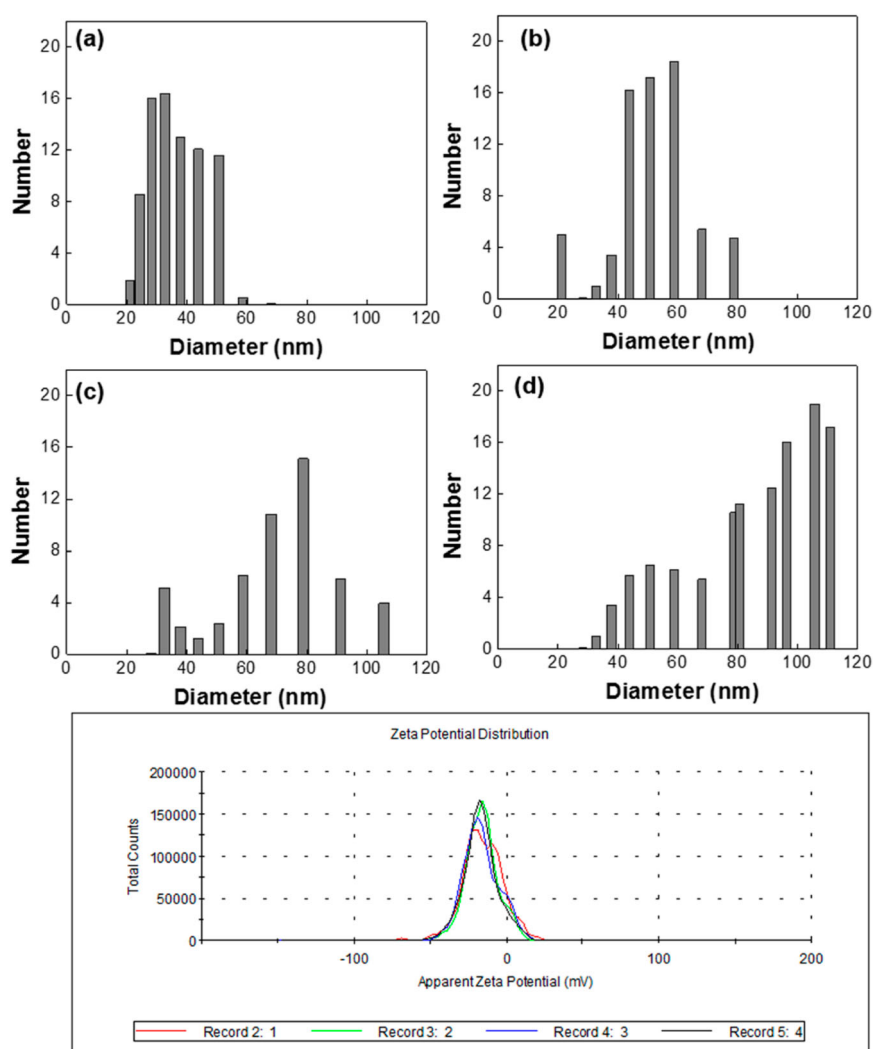


Figure 2. DLS (a–d) and zeta potential (e) results of samples prepared with different weight ratios of starch to AgNO_3 : (a) 1.5, (b) 2, (c) 5, and (d) 10.

2.3. Antibacterial activity

The bacterial cultures were obtained from the Korean Culture Center of Microorganisms (KCCM), Republic of Korea. Specific strains used were Gram-positive bacteria *B. cereus* ATCC13061, *S. aureus* ATCC6538p, *S. saprophytic* KCTC3345, and *L. monocytogenes* ATCC7644; and Gram-negative bacteria *E. coli* KCTC1682, *P. vulgaris* KCTC2512, *P. putida* ATCC49128, and *S. typhi* KCCM11862. All bacterial strains were maintained on Tryptic Soy Agar plates at 4°C up to 3 months, and stocks were preserved at -80°C in 30% glycerol containing Tryptic Soy Broth medium.

Bacterial culture dilution adjusted to 0.08–0.1 optical density at 625 nm and 100 µl was spread on pre-incubated Mueller and hinton agar (MHA) plates with the help of a sterile glass rod. The 8 mm wells were prepared with the help of a cork borer and 100 µl of Ag₂O nanoparticle solution (100 µg/ml in water) was poured and plates were incubated at 37°C for 24 h. Ampicillin (100 µg/ml water) was used as a positive control. After incubation, the zone of inhibition (ZOI) was measured in mm of diameter. All experiments were carried out in triplicates.

3. Results and discussion

Starch has been receiving increasing attention because it can be employed as a non-toxic and environmentally benign stabilizing agent for nanoparticle syntheses. In particular, the multiple hydroxy groups present in the glucose unit of starch molecule facilitate the complexation with metal oxide nanoparticles. In this study, it was found that Ag₂O nanoparticles can be prepared by simply stirring a mixture solution consisting of starch and AgNO₃ at room temperature without any additional chemicals. Starch as a biopolymer has variable molecular weight, so it is convenient to express the weight ratio with respect to AgNO₃. Here, the weight ratio of starch to AgNO₃ was adjusted in the range of 1.5–10, which has been found to strongly influence the structural characteristics of synthesized nanoparticles. It was further noted that pHs of starch solution before and after the addition of AgNO₃ were 6 and 5, respectively.

It was observed that the color of the reaction mixture changed from initial transparent to yellow and then brown with stirring, which could be a good indicator of a successful synthesis of Ag₂O nanoparticles. The color of reaction mixture changed after 3 h, that is transparent to yellow, and after 5 h it changed to brown, indicating that the reaction rate was very slow. Having observed the color change, the synthesized Ag₂O nanoparticles have been further analyzed by different experimental

techniques. At first, structural features of the nanoparticles were characterized by TEM. As shown in Figure 1, Ag₂O nanoparticles have relatively broad diversity in size and shape, while spherical and circular disc-shaped nanoparticles are present in a large degree. Nevertheless, a gradual growth in the size of nanoparticles can be discernible along with the increase in weight ratios of starch to AgNO₃ (Figure 1(a)–(d)). It would also be worthwhile to note that the shape of nanoparticles is more or less circular disc in Figure 1(a) and 1(b), but become mostly faceted in Figure 1(c) and 1(d). In general, the reaction rate is proportional to the concentration of reactant. In this context, the reaction rate in Figure 1(a) and 1(b) having low starch contents would be slower than those in Figure 1(c) and 1(d); this indicates that the formation of circular disc-shaped nanoparticles is more favorable under a slow reaction condition. It is to be noted that this behavior might be comparable to those previously found in the synthesis of metal nanoparticles. In the case of shape-controlled synthesis of metal nanoparticles, slow reduction allows the formation of plate-shaped nanoparticles by kinetic reason while fast reduction favors thermodynamically stable faceted structures (18, 19).

To better examine the size distribution of nanoparticles, the hydrodynamic diameter of nanoparticles was further analyzed by dynamic light scattering (DLS). When the weight ratio of starch to AgNO₃ was 1.5, relatively uniform nanoparticles with an average diameter of 40.6 nm have been obtained (Figure 2(a)). As the weight ratio was adjusted to 2.0, the size of nanoparticles slightly

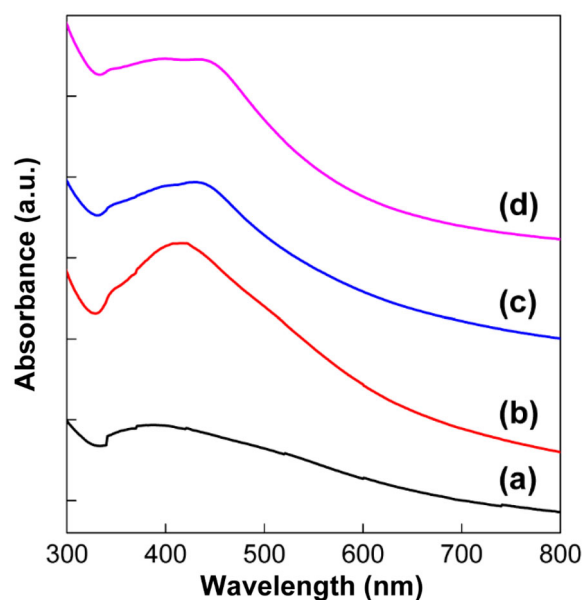


Figure 3. UV-Vis spectra of samples prepared with different weight ratios of starch to AgNO₃: (a) 1.5, (b) 2, (c) 5, and (d) 10.

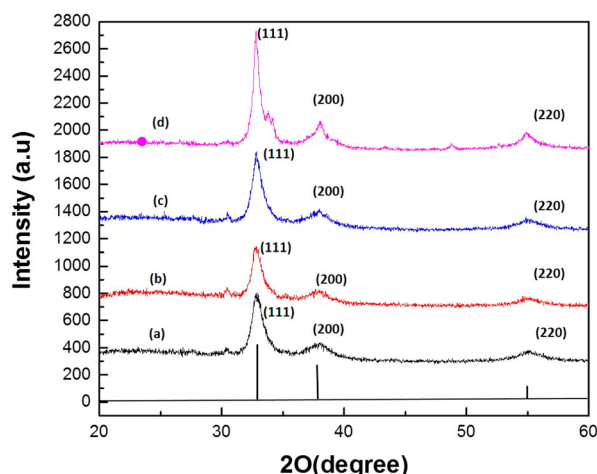


Figure 4. Typical XRD pattern of samples prepared with different weight ratios of starch to AgNO_3 : (a) 1.5, (b) 2, (c) 5, and (d) 10.

increased with an average diameter of 55.8 nm, as shown in Figure 2(b). Further increase in the weight ratios to 5.0 (Figure 2(c)) and 10.0 (Figure 2(d)) resulted

in the larger diameters with average values of 62.4 and 78.6 nm, respectively. Along with the increase in the diameter, the aggregation among nanoparticles becomes more severe, as shown in Figure 1. In addition, zeta potentials of the Ag_2O nanoparticles were measured as -15.02 mV (Figure 1(a)), -16.10 mV (Figure 1(b)), -16.81 mV (Figure 1(c)), and -16.71 mV (Figure 1(d)), respectively, indicating more or less stable nanoparticles.

In parallel, optical properties of Ag_2O nanoparticles were investigated by UV-Vis spectroscopy. All the synthesized nanoparticles from different starch contents exhibited a broad peak in the range of 350–600 nm (Figure 3) (20). As in the previous results, the weight ratios of starch to AgNO_3 were adjusted to 1.5, 2, 5, and 10 for (a), (b), (c), and (d), respectively. Even though the absorption spectra appear quite similar to each other, one can find the gradual broadening and red shifts in the absorption spectra from Figure 3(a) to 3(d); this could be ascribed to the increased diameter and/or aggregation of nanoparticles, as discussed in TEM and DLS results (Figures 1 and 2).

Table 1. All values were taken from triple individual experiments and expressed as average, \pm error indicates standard deviation.

Organism	ZOI (mm)				Ampicillin (100 $\mu\text{g}/\text{ml}$)
	Sample a	Sample b	Sample c	Sample d	
<i>B. cereus</i>	11	13	14	15	21
<i>S. aureus</i>	13	14	16	17	22
<i>S. saprophyticus</i>	0	12	13	14	23
<i>L. monocytogenes</i>	10	12	13	15	20
<i>E. coli</i>	0	11	12	13	19
<i>P. vulgaris</i>	0	0	9	10	17
<i>P. putida</i>	14	15	17	19	21
<i>S. typhi</i>	12	14	15	16	20

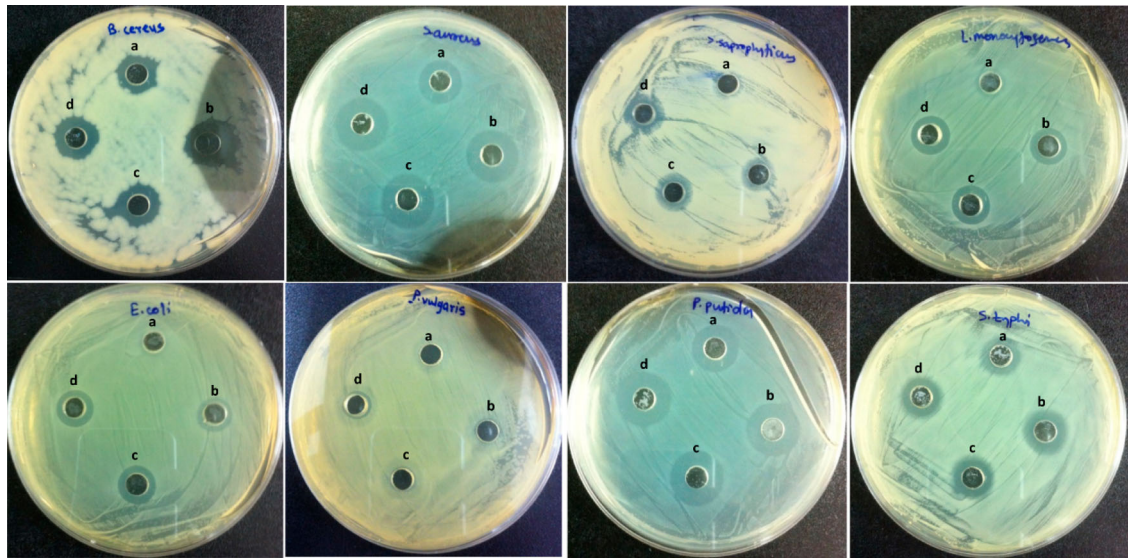


Figure 5. Bacterial cultures shows the inhibition zone of Ag_2O nanoparticles around the wells on plates containing different strains of bacteria (sequence from left top to right bottom; *B. cereus*, *S. aureus*, *S. saprophyticus*, *L. monocytogenes*, *E. coli*, *P. vulgaris*, *P. putida*, *S. typhi*).

To further identify the structure of the synthesized nanoparticles, XRD patterns have been collected and are shown in Figure 4. Basically, all the nanoparticles exhibited the same pattern which matches the JCPDS data of Ag₂O lattice (JCPDS. No 41-1104), confirming the formation of Ag₂O nanoparticles. The XRD diffraction patterns shown in Figure 4 were in good agreement with the earlier research reported for the synthesis of Ag₂O nanoparticles. No other phases were observed, indicating the purity of Ag₂O nanoparticles. When the sizes of Ag₂O crystal were determined by Debye-Scherrer equation, they were (a) 4.08 nm, (b) 5.09 nm, (c) 5.4 nm, and (d) 10.82 nm, respectively. It is to be noted that these values from XRD results are much smaller than those obtained from TEM and DLS measurements, which could be ascribed to polycrystalline nature of the prepared Ag₂O nanoparticles.

After the structural characterization, the antibacterial properties of Ag₂O nanoparticles have been tested by performing the well-diffusion method against various bacterial cultures, as listed in Table 1. Briefly, diluted bacterial cultures were spread on MHA plates. Subsequently, four wells were prepared by a cork borer, onto which the Ag₂O nanoparticles synthesized from different starch concentrations (labeled as (a)–(d) in each plate in Figure 5) have been applied. As confirmed from Figure 5, after incubating at 37°C for 24 h, the bacterial cultures clearly exhibited a circular hole around each well, in which bacterial activity had been inhibited by Ag₂O nanoparticles. It is to be noted that the food pathogens were susceptible to all Ag₂O samples. Sample (a) was unable to inhibit the growth of *S. saprophyticus*, *E. coli*, and *P. vulgaris*, while sample (b) did not show any activity against *P. vulgaris*. Samples (c) and (d) showed good antibacterial activity against all tested food pathogenic bacteria. All Gram-positive bacteria showed more susceptibility with respect to Gram-negative bacteria. The ZOI that represented antibacterial susceptibility was observed to gradually increase from samples (a) to (d), as the size of Ag₂O nanoparticles increased. It may be possible that antibacterial susceptibility depends on particle size. The present study results of Ag₂O activity as an antibacterial agent is compatible with a previous study (21).

4. Conclusions

In this study, a simple and versatile approach for the synthesis of Ag₂O nanoparticles has been developed. Using this method Ag₂O nanoparticles can be directly synthesized by stirring a mixture solution consisting of starch and AgNO₃ at room temperature without any addition of other toxic chemicals. With increasing

weight ratio of starch to AgNO₃, the average diameter of Ag₂O nanoparticles gradually increased, which has been accompanied by noticeable morphological transition from spherical and circular shapes to more faceted structures. In addition, the synthesized Ag₂O nanoparticles exhibited substantial antibacterial activity against food pathogenic Gram-positive and Gram-negative bacteria.

Disclosure statement

No potential conflict of interest was reported by the authors.

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