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Effect of Silver Nitrate Precursor Concentration on the Structural and Morphological Properties of Ag₂O Nanoparticles Synthesized by the Sol-Gel Method

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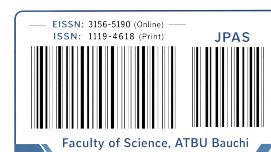
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Abstract

Silver oxide (Ag₂O) nanoparticles have been synthesized by simple sol-gel method using different concentrations of silver nitrate (AgNO₃) (0.5 M and 1.0 M) and then calcined at 250 °C. This work has focused on the effect of the precursor concentration on the phase, crystallinity and morphology of the product. The X-ray diffraction (XRD) analysis confirmed the formation of a single phase - the cubic structure of Ag₂O (space group Pn-3m, JCPDS card no. 41-1104) and revealed that both the samples exhibited the characteristic (111), (200), (220), (311) and (222) reflections. The intensity and sharpness of the diffraction peaks increased with the concentration of the sample and the average crystallite size estimated by the Scherrer equation was found to be 0.5 M (approx. 21.8 nm) and 1.0 M (approx. 30.7 nm) respectively, which showed that the higher the concentration the better the crystallinity. Field-emission scanning electron microscopy (FE-SEM) showed almost spherical, cauliflower-like agglomerates with the measured feature sizes ranging from about 44 to 72 nm, and which increased as the precursor concentration increased. It was observed that only silver and oxygen were present by energy-dispersive X-ray (EDX) analysis, and the ratio of Ag:O was found to be about 2:1, suggesting the presence of Ag₂O. The elemental maps revealed the uniform distribution of both elements without any trace of other impurities. The Fourier Transform Infrared (FTIR) spectrum exhibited a prominent band of metal-oxygen stretching around 540 cm⁻¹ corresponding to Ag-O stretching, and weaker bands due to the surface hydroxyl groups, adsorbed water, and residual nitrate species. The results show that the concentration of the precursor is an easy and effective parameter to control the crystallite size and crystallinity of the sol-gel Ag₂O nanoparticles at low calcination temperature.

Keywords

Silver Oxide;
Ag₂O Nanoparticles;
Sol-Gel Method;
Silver Nitrate;
Precursor Concentration;
X-ray Diffraction;
Crystallite Size;
FTIR.



1. Introduction

Metal-oxide nanoparticles have become one of the most intensively studied classes of functional materials because their properties can differ dramatically from those of the corresponding bulk solids. As the particle size falls into the nanometre range, the large surface-to-volume ratio and the appearance of size-dependent electronic states give rise to optical, catalytic, electrical, and antibacterial behaviour that is not seen at larger scales [1], [4], [5]. Among these oxides, silver oxide (Ag_2O) has attracted growing attention because it combines a narrow semiconducting band gap with the well-known biological activity of silver, which makes it attractive for photocatalysis, gas sensing, energy storage, and antimicrobial applications [3], [5], [13].

Silver(I) oxide crystallises in a cubic cuprite-type structure, the space group Pn-3m , and each silver ion is linearly coordinated by two oxygen atoms, while each oxygen atom is at the centre of an Ag_4 tetrahedron [6]. The crystallinity and phase purity of Ag_2O is rather sensitive to the preparation condition because this relatively open structure with an easy reduction of Ag^+ allows this. Several different approaches have been tried to prepare it, such as the chemical precipitation, green (plant-mediated), electrochemical deposition, solvothermal process and sol-gel process [2] and [8,9] and [11-14]. All of these methods provide a different level of simplicity, cost, and control of particle size.

The sol-gel method is especially attractive for oxide nanoparticles because it involves solution chemistry, has low process temperature, and offers a good degree of molecular mixing and a means of controlling the final microstructure by varying such parameters as precursor concentration, pH, and calcination temperature [7, 15]. In reality, the concentration of the metal-salt precursor is the most convenient parameter to change, because it directly controls the degree of supersaturation at the gelation point and, therefore, the nucleation/growth balance during gelation, which in turn determines the final

crystallite size [15]. Nevertheless, systems studies which retain the calcination conditions constant, while varying the AgNO_3 concentration to study the effect on the structure of sol-gel Ag_2O are still relatively scarce.

The method adopted in the present work was sol-gel method and two different concentrations of silver nitrate solution (0.5 M and 1.0 M) were used for the synthesis of Ag_2O nanoparticles at a moderate calcination temperature of 250 °C. The objective was to investigate the effect of the concentration of the precursor on the phase formation, crystallite size, crystallinity, morphology and chemical composition of the powders in a controlled manner. The X-ray diffraction, field-emission scanning electron microscopy and energy-dispersive X-ray analysis were used to characterize the samples and the trends across the two concentrations are discussed with the framework of classical nucleation-and-growth arguments.

2. EXPERIMENTAL WORK AND MATERIALS USED

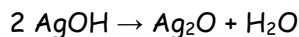
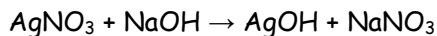
2.1 MATERIALS

Silver nitrate (AgNO_3 , analytical grade, $\geq 99\%$) was used as the silver precursor. Sodium hydroxide (NaOH) was used for adjusting pH and hydrolysis, absolute ethanol and deionised water were used as solvents and as washers. All chemicals used in the experiment were analytical reagent grade and were used without further purification.

2.2 Synthesis of Ag_2O nanoparticles

The nanoparticles of Ag_2O were synthesized using sol-gel method as described by recent reports on silver-based oxides [1, 2, 11, 14]. Silver nitrate was dissolved in deionised water to obtain two different precursor solutions with final concentrations of 0.5 M and 1.0 M, respectively. Solutions were stirred on a magnetic stir at approximately 60 °C for 30 min and a clear homogeneous solution obtained. A dilute solution of NaOH was then added dropwise, stirring constantly, so

that the pH went into the alkaline range ($\text{pH} \approx 11$). Upon addition of the base immediately a brownish-grey suspension was formed, which is indicative of hydrolysis of Ag^+ and the formation of unstable silver hydroxide intermediate which spontaneously turns to silver oxide as summarized below: [2,11].



The sol was stirred for an additional 2 h at the same temperature so that it develops and slowly gels. The resulting precipitate was aged before being collected by centrifugation and washed a number of times with deionised water and with ethanol to remove the sodium, unreacted nitrate ions and other soluble by-products. The washed gel was dried in an oven with a temperature of approximately 80°C for overnight period and a dark powder was obtained. Finally, the dried powder was calcined at 250°C for 1 h in a muffle furnace to complete the crystallisation of the cubic Ag_2O phase and to remove any remaining organic and nitrate species [1, 14]. This was performed on both concentrations of the precursor and the two products are referred to in this text as the 0.5 M and 1.0 M samples.

3. Characterization Techniques

The crystal structure and phase purity of the calcined powders were examined by X-ray diffraction (XRD) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of

20° – 80° . The average crystallite size was estimated from the most intense reflections using the Debye-Scherrer equation [10], [12], [16]. The particle morphology was investigated with a field-emission scanning electron microscope (FE-SEM, TESCAN MIRA3), and the elemental composition together with the elemental distribution was obtained from the coupled energy-dispersive X-ray (EDX) detector and the corresponding elemental maps. The functional groups and metal-oxygen bonding were identified by Fourier-transform infrared (FTIR) spectroscopy recorded in the range 400 – 4000 cm^{-1} .

4. RESULTS AND DISCUSSION

4.1 X-ray diffraction analysis

Figure. 1 shows the XRD patterns of the Ag_2O nanoparticles prepared with 0.5 M and 1.0 M silver nitrate and calcined at 250°C . Both patterns display the set of reflections expected for the cubic cuprite-type Ag_2O structure (space group $\text{Pn}\bar{3}\text{m}$), and the peak positions match the standard JCPDS card no. 41-1104 [6]. The diffraction peaks located at $2\theta \approx 32.74^\circ$, 38.12° , 54.94° , 65.41° , and 69.66° are indexed to the (111), (200), (220), (311), and (222) planes of Ag_2O , respectively. The absence of any additional reflections indicates that single-phase Ag_2O was obtained under these conditions and that the calcination temperature of 250°C was sufficient to crystallise the oxide without decomposing it to metallic silver [1], [5].

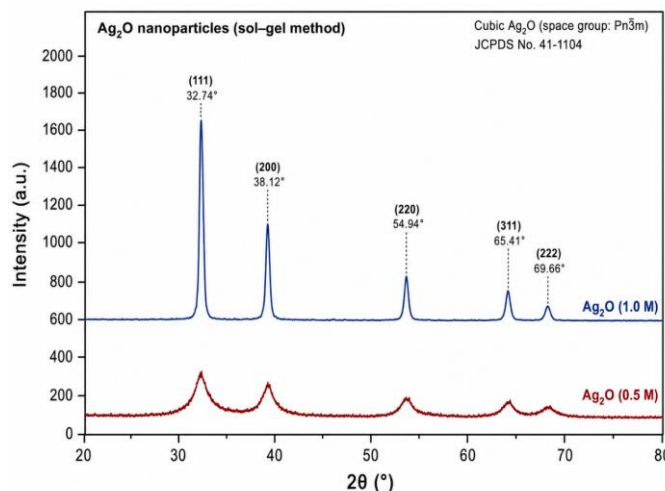


Figure. 1. XRD patterns of Ag_2O nanoparticles synthesised by the sol-gel method with 0.5 M and 1.0 M AgNO_3 precursor and calcined at 250°C , indexed to cubic Ag_2O (JCPDS 41-1104).

The samples can clearly be distinguished from each other. The reflections are sharp and strong for the 1.0 M sample but are much broader and weaker for the 0.5 M sample. The peaks in this size range are broader due to the finite crystallite dimension and the sharper peaks for the 1.0 M sample indicate larger crystallites that are more developed and have a higher crystallinity. This behaviour is consistent with a nucleation-and-growth picture: at the higher precursor concentration there is more of the silver species in the solution and the growth of the crystallites is more favoured as compared to the nucleation of new crystallites and therefore the average crystallite is larger [15].

The average crystallite size D was calculated using the Scherrer equation $D = K\lambda / (\beta \cos \theta)$, in which $K \approx 0.9$ is the shape factor, λ is the X-ray wavelength, β is the full width at half maximum of the reflection in radians and θ is Bragg angle [10, 16]. The results are summarised in Figure. 2. For all the reflections the full width at half maximum decreases systematically as the sample number increases from 0.5 M to 1.0 M, and the crystallite size increases in a similar fashion. The average crystallite size of the sample of 1.0 M increases from about 21.8 nm to 30.7 nm as compared to the 0.5 M sample. The values are well below the average of about 15 nm to 40 nm range reported for Ag_2O nanoparticles synthesized using similar wet chemical methods [2, 3, 6].

Table 1: XRD parameters (2θ , Miller indices, FWHM, d-spacing, and Scherrer crystallite size) for the 0.5 M and 1.0 M Ag_2O samples, together with the average crystallite size for each concentration

Sample	2θ (°)	Miller Index (hkl)	FWHM (°)	d-spacing (nm)	Crystallite Size (nm)
0.5 M	32.74	(111)	0.47	0.2733	17.62
0.5 M	38.12	(200)	0.44	0.2359	19.10
0.5 M	54.94	(220)	0.41	0.1670	21.84
0.5 M	65.41	(311)	0.39	0.1426	24.21
0.5 M	69.66	(222)	0.37	0.1349	26.16
1.0 M	32.74	(111)	0.34	0.2733	24.35
1.0 M	38.12	(200)	0.32	0.2359	26.27
1.0 M	54.94	(220)	0.29	0.1670	30.88
1.0 M	65.41	(311)	0.27	0.1426	34.97
1.0 M	69.66	(222)	0.26	0.1349	37.22
Average crystallite size for 0.5 M				21.78 nm	
Average crystallite size for 1.0 M				30.74 nm	

4.2 Morphological and compositional analysis (FE-SEM/EDX)

Two samples have been analyzed by using the FE-SEM, to which EDX has been used, and the results can be seen in Figure. 2 (0.5 M) and Figure. 3 (1.0 M) respectively. In both instances the powders are composed of grains which are almost spherical and

have a cauliflower-like shape, and which tend to form larger aggregates. An aggregated, rounded morphology is typical for solution-synthesized Ag_2O nanoparticles and is typically thought to be caused by the high surface energy of the fine crystallites which tend to coalesce in order to decrease the total surface area [2, 11].

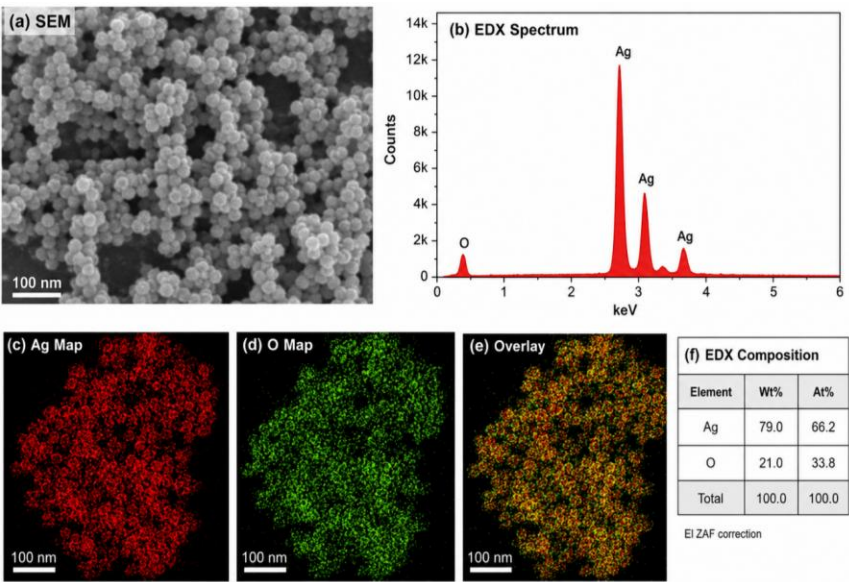


Figure. 2. FE-SEM image, EDX spectrum, elemental maps (Ag and O), overlay, and quantitative EDX composition of the Ag_2O nanoparticles prepared with 0.5 M AgNO_3 .

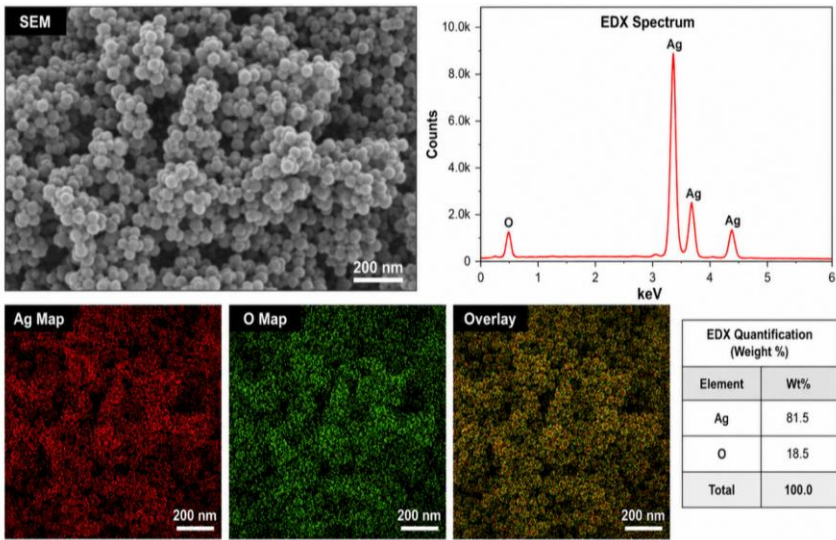


Figure. 3. FE-SEM image, EDX spectrum, elemental maps (Ag and O), overlay, and quantitative EDX composition of the Ag_2O nanoparticles prepared with 1.0 M AgNO_3 .

The EDX spectra of both samples indicate that the product is chemically pure, with no signals from foreign elements, demonstrating that the washing steps were able to effectively remove sodium and residual nitrate. The measured weight percents (approx. 79% Ag, 21% O for the sample 0.5 M and approx. 81.5% Ag, 18.5% O for the sample 1.0 M) are near the stoichiometric composition of Ag_2O and are fairly consistent with the

XRD identification of a single phase of pure silver-oxide [1] and [6]. The elemental maps of Ag and O are nearly identical and the overlay of these maps shows that both elements are evenly distributed throughout the particles, not segregated, further evidence of a single-phase oxide that is homogeneous.

Higher-magnification FE-SEM micrographs of the two samples are compared in Figure. 4 and Figure. 5.

The individual features measured on these images grow from roughly 44–48 nm for the 0.5 M sample to about 68–72 nm for the 1.0 M sample. The same trend seen in the XRD data larger building blocks at the higher precursor concentration is therefore reproduced in the electron-microscopy images. The

particle sizes observed by FE-SEM are somewhat larger than the crystallite sizes obtained from the Scherrer analysis, which is expected because each SEM grain is generally made up of several coherently diffracting crystallites, and because agglomeration adds to the apparent feature size [12], [16].

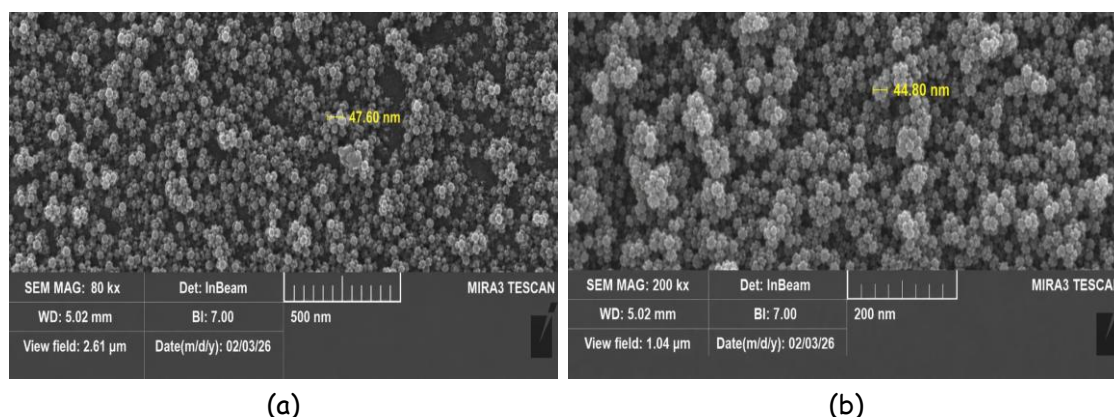


Figure. 4. FE-SEM micrographs of the 0.5 M Ag_2O sample at (a) 80 kx and (b) 200 kx magnification, with representative feature sizes marked.

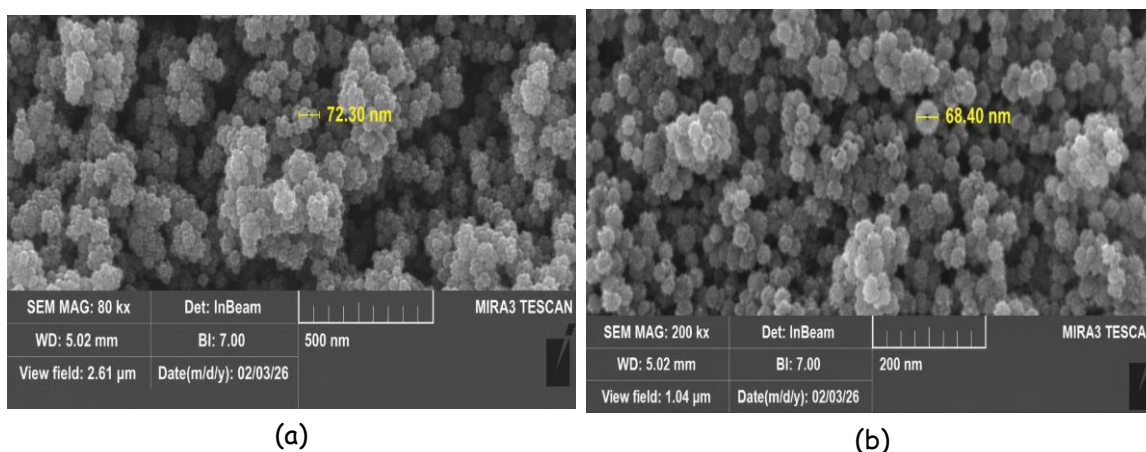


Figure. 5. FE-SEM micrographs of the 1.0 M Ag_2O sample at (a) 80 kx and (b) 200 kx magnification, with representative feature sizes marked.

4.3 FTIR analysis

The FTIR spectra of the two Ag_2O samples are shown in Figure. 6, and the band assignments are listed in Table 1. The most important feature for confirming the formation of the oxide is the strong absorption

band located in the $536\text{--}548\text{ cm}^{-1}$ region, which corresponds to the Ag-O metal-oxygen stretching vibration and is the fingerprint of the Ag_2O lattice [1], [6], [11]. This band is more pronounced for the 1.0 M sample, in line with its higher crystallinity as deduced from XRD.

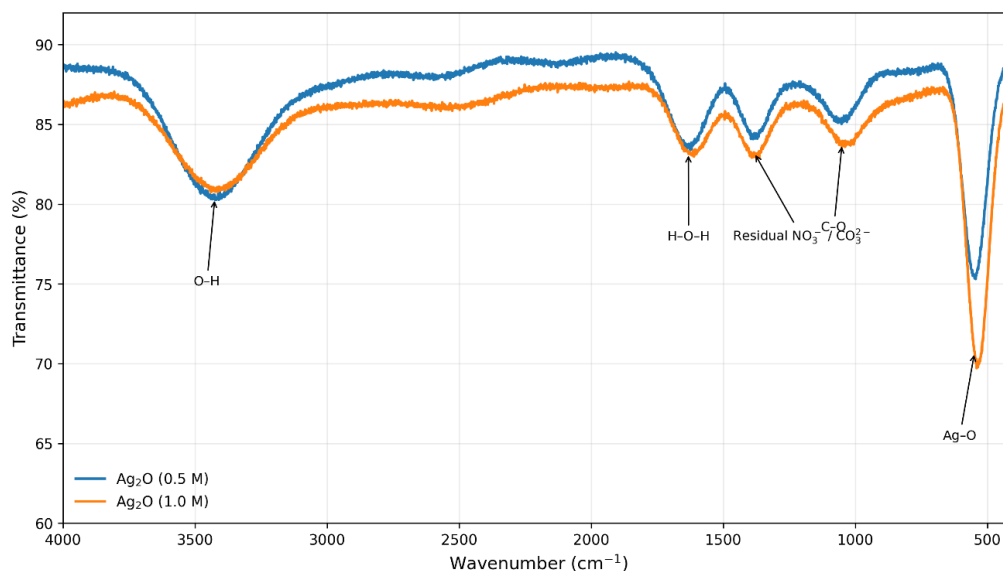


Figure. 6. FTIR spectra of the sol-gel Ag_2O nanoparticles prepared with 0.5 M and 1.0 M AgNO_3 , showing the characteristic Ag-O band together with surface-related bands.

The others bands have been correlated with species that are adsorbed on the surface of the nanoparticles or with residues of the precursors. The broad absorption around $3408\text{--}3425\text{ cm}^{-1}$ is attributed to the O-H stretching mode of the hydroxyl groups on the surface and the physically adsorbed water molecules, while the band around $1624\text{--}1632\text{ cm}^{-1}$ is attributed to the bending mode of physically adsorbed water molecules. The weak feature at $1381\text{--}1384\text{ cm}^{-1}$

can be assigned to the residual nitrate ions or surface carbonate on the aerated sample, while the feature around $1038\text{--}1050\text{ cm}^{-1}$ is assigned to the small amounts of residual organic species from the sol-gel precursors [7, 15]. Only weak surface bands are left, together with the strong Ag-O signal, which demonstrates that the calcination step resulted in a reasonably pure silver oxide phase.

Table 2. FTIR band assignments for the sol-gel Ag_2O nanoparticles.

Wavenumber (cm^{-1})	Bond / Group	Vibrational mode	Interpretation
3408-3425	O-H	Stretching	Surface hydroxyl groups and adsorbed water
1624-1632	H-O-H	Bending	Physically adsorbed water molecules
1381-1384	$\text{NO}_3^- / \text{CO}_3^{2-}$	Symmetric stretching	Residual nitrate ions or surface carbonate species
1038-1050	C-O	Stretching	Residual organic species from the sol-gel precursors
536-548	Ag-O	Metal-oxygen stretching	Confirms the formation of silver oxide, Ag_2O

5. CONCLUSIONS

Single-phase cubic Ag₂O (space group Pn-3m, JCPDS 41-1104) without secondary phases were successfully obtained by a simple sol-gel method from the silver nitrate precursor solutions and further calcination at 250 °C, which is a comparatively low temperature, sufficient to crystallise the oxide. The higher concentration of AgNO₃ (0.5M to 1.0M) sharpened and intensified the diffraction peaks as well as increased the average crystallite size from ~21.8nm to ~30.7nm, which was consistent with a growth favoured nucleation model for higher supersaturations.

FE-SEM showed almost spherical cauliflower like agglomerates of feature sizes which increased from ~44-48 nm to ~68-72 nm with concentration, which is in agreement with the XRD result, and EDX showed a pure Ag-O composition, close to the Ag₂O stoichiometry, with a homogeneous elemental distribution. The presence of oxides was confirmed by FTIR with the characteristic vibration of Ag-O stretching band around 540 cm⁻¹ with weak bands corresponding to surface groups. Overall, these findings demonstrate that the concentration of the precursor is a simple yet effective parameter to control the crystallite size and crystallinity of the sol-gel derived Ag₂O nanoparticles, which can be exploited for tuning the material for photocatalytic, sensing, and antibacterial applications.

COMPETING INTERESTS

The author declares no competing financial or nonfinancial interests or personal relationships with other people or organizations that could have influenced the work covered in the current article.

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