

Green, Rapid and Facile HPMo-Assisted Synthesis of Silver Nanoparticles

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Abstract: In the present paper, we have described the interesting behavior of molybdophosphoric acid ($H_3[PMo_{12}O_{40}]$, HPMo) in the size-controlled synthesis of silver nanoparticles under UV-irradiation. In this process which is based on the reduction of Ag^+ ($AgNO_3$), HPMo plays the role of photocatalyst, reducing agent as well as stabilizer, and propan-2-ol acts as a sacrificial agent. The method allows the rapid synthesis of uniform spherical nanoparticles with an average size that varies between 2.2 and 35.2 nm by altering the silver ion concentration, molar ratio of silver ion to HPMo (or dose of HPMo) and Propan-2-ol amount. It is found that there is a critical ratio for $[Ag^+]/[HPMo]$ (i.e. 3.8 in the present case), in which two opposing trends in the size of silver nanoparticles take place.

Keywords: Molybdophosphoric acid, polyoxometalate, silver, nanoparticle, UV irradiation.

1. INTRODUCTION

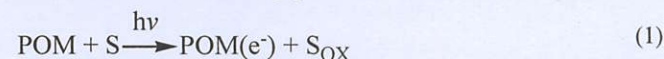
In recent years, silver nanoparticles (Ag NPs) have been extensively investigated due to their unique physical, electrical and chemical properties, which offer them many applications in chemical medicine, industry, electronics, etc. Several chemical and physical methods have been used to prepare these nanoparticles [1]. However, finding a method in which one could control and select the size of the prepared nanoparticles is of great interest in order to maximize particles efficiency. Manipulating size of nanoparticles can be achieved through the control of nucleation and growth steps by varying the synthesis parameters, including activity of the reducing agents, type and concentration of the precursors, and also nature and amount of the protective agents [2, 3].

Among all preparation methods, the chemical reduction of silver ions in the presence of a protecting agent is the most widespread way [4]. Common reductants are elemental hydrogen, citrate, ascorbate, and borohydride [5-7], although in recent years, organic and inorganic bases are also used in the reaction [4, 5, 7]. Based on the green chemistry principles, the green synthesis of Ag NPs involves selection of an eco-friendly solvent and environmentally benign reducing agent [1]. However, currently most of the employed reductants are against the principles of green chemistry.

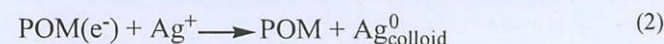
Recently, it has been reported that polyoxometalates (POMs), as a unique class of molecularly defined inorganic metal-oxide clusters, can act as reducing agent in the preparation of metal nanoparticles [8-12]. POMs are promising candidates for green materials, as they are harmless to the environment with respect to corrosiveness, safety, quantity of waste and separability. Other key green aspects of solid POMs are related to their synthesis in an aqueous process and achievements of successful practical applications.

Moreover, POMs have unique properties such as: strong Bronsted acidity, high hydrolytic stability (in the pH range 0-12), high thermal stability, operating in pure water without any additive, and non-corrosiveness [13, 14]. POM's structures remain unchanged under stepwise and multielectron redox reactions and can be reduced by photochemical and electrochemical procedures using suitable reducing agents [15, 16].

POMs have been used as both reducing agents and stabilizers for the synthesis of metal nanoparticles such as Ag, Au, Pt, and Pd upon illumination with UV/near-Vis light [9]. POMs can be reduced in the presence of oxidizable organic substrates (S) like alcohols, under UV irradiation [9]:



Then, in the reduced form, POMs would reduce metal ions to their corresponding metal nanoparticles. For example, in the case of silver ion, the following equation represents the reaction:



There are several reports regarding synthesis of Ag NPs using the above mentioned process. Troupis *et al.* used the photocatalytic process for Ag NPs synthesis in the presence of $H_4[SiW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]$ as Keggin types and $H_6[P_2W_{18}O_{62}]$ as Dawson type of POM [8, 9]. Also, other researchers have used these Keggin types of POM [17, 18] and Mo^V - Mo^VI mixed-valence POMs [19] in the preparation of Ag NPs and Ag nanorods [20]. Moreover, Mandal *et al.* have synthesized Ag NPs [18] and more complicated nanostructures such as Au-Ag core-shell dimetallic compounds [21].

Although, Keggin, mixed-valence and Dawson types of POMs have been used in the synthesis of Ag NPs, to the best of our knowledge, the role of molybdophosphoric acid ($H_3[PMo_{12}O_{40}]$, HPMo) has been largely overlooked and there is no report using this type of POM. Furthermore, among the various Keggin type of POMs, HPMo has the highest oxidation potential [22], which can help in synthesizing smaller and more uniform nanoparticles via rate-redox process.

In continuation of our recent works in the area of green synthesis of metal nanoparticles using POMs [11, 12, 23-25], in the present work we have used Molybdophosphoric acid as a green photocatalytic reducing agent and stabilizer to synthesis silver nanoparticles via a simple and efficient photoreduction technique at ambient temperature. Besides, the effect of silver ion concentration, dose of HPMo (or molar ratio of silver ion to HPMo) and propan-2-ol amount have also been investigated.

2. MATERIALS AND METHODS

2.1. Chemicals and Apparatus

All the chemicals were obtained from Merck Company and used as received. UV visible spectra were obtained using Avantes

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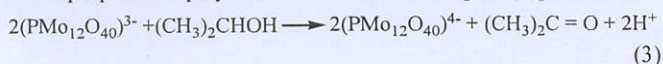
Avaspec-3648 single beam instrument. The synthesized Ag NPs were characterized mainly by its particle size distribution using a ZetaSizer Nano ZS apparatus (Malvern Instruments Ltd.) as a laser particle sizer. The instrument allowed to measure particle size taking the advantage of optoelectronic systems. Also, nanoparticles were characterized using Transmission Electron Microscopy (Philips CM-120).

2.2. Synthesis of Ag NPs

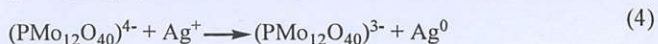
In a typical experiment, 5 mL of an aqueous solution of HPMo (with a determined concentration), 10 mL AgNO_3 (0.25×10^{-4} to 10^{-3} M) and 2 mL propan-2-ol were placed into a spectrophotometer cell and deaerated with N_2 gas for 15 min. Then, the mixture was irradiated by UV light (125 W high pressure mercury vapor lamp) under continuous stirring. Reaction was performed at a constant room temperature, using water circulating around the cell. The color of the solution changed from colorless to yellow or brown (based on the particle size of nanoparticles), indicating the formation of Ag NPs. The nanoparticles were separated by a high speed centrifuge (14000 rpm), and washed twice with water.

3. RESULTS AND DISCUSSION

HPMo as a Keggin structure, was chosen to study the synthesis of Ag NPs in a reaction between the reduced HPMo ($[\text{PMo}_{12}\text{O}_{40}]^{4-}$) and Ag^+ ions. The $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ ion was obtained by photolysis of a deaerated aqueous solution of propan-2-ol and $(\text{PMo}_{12}\text{O}_{40})^{3-}$, in which propan-2-ol plays the role of sacrificial agent (Equation 3).



After reduction, the color of the solution turned gradually to yellow (formation of Ag^0), due to the ability of reduced HPMo ($[\text{PMo}_{12}\text{O}_{40}]^{4-}$) for transferring electrons efficiently to silver ions.



The above two equations were occurred in a one-pot system at ambient temperature. HPMo ions can be utilized cyclically as oxidizing or reducing agent according to equations 3 and 4. The process was monitored by the visible absorption spectrometry.

Fig. (1) shows the UV/Vis spectra of the mixture of HPMo (1.3×10^{-4} M), AgNO_3 (5×10^{-4} M) and propan-2-ol at different stages of treatment. It can be seen that before irradiation, there is not any distinct absorption band in the wavelength range of 400-800 nm. However, just after 15 min UV irradiation, the absorption bands were observed in the SPR band of silver NPs at about 430 nm. These absorption bands that were caused by the excitation of surface-plasmon vibrations, indicate formation of Ag NPs. From this figure, it can be observed that the absorption band becomes sharper and the resonance intensity increases due to the increased number of Ag NPs during the process in a short time. Fig. (1) also shows that within the first 3 min of irradiation, there is no absorption band at 430 nm indicating no formation of Ag NPs. In this distance, the Ag NPs production rate (equation 4) is negligible and equation 3 is in progress.

The synthesized nanoparticles were apt to aggregate and precipitate in the solution due to their typical hydrophobic surface property. Some researchers have shown the stabilizer role of POMs in the synthesis of metal nanoparticles [8-10]. Also, we observed that in the absence of HPMo, Ag NPs were precipitated after a short time, but in the presence of HPMo, the resulting colloid was stable without any precipitating for several weeks. These observations indicate the stabilizing role of HPMo in this reaction. This might be due to the POM polyanions adsorbing onto the surface of Ag NPs which provide both kinetic stabilization, through coulombic repulsion between the negatively charged particles, and also steric stabilization [10]. Therefore, it is concluded that HPMo is an excellent stabilizer to prevent agglomeration. Besides, it is easily rinsed after the reaction by washing with water and will not contaminate the nano silver particles.

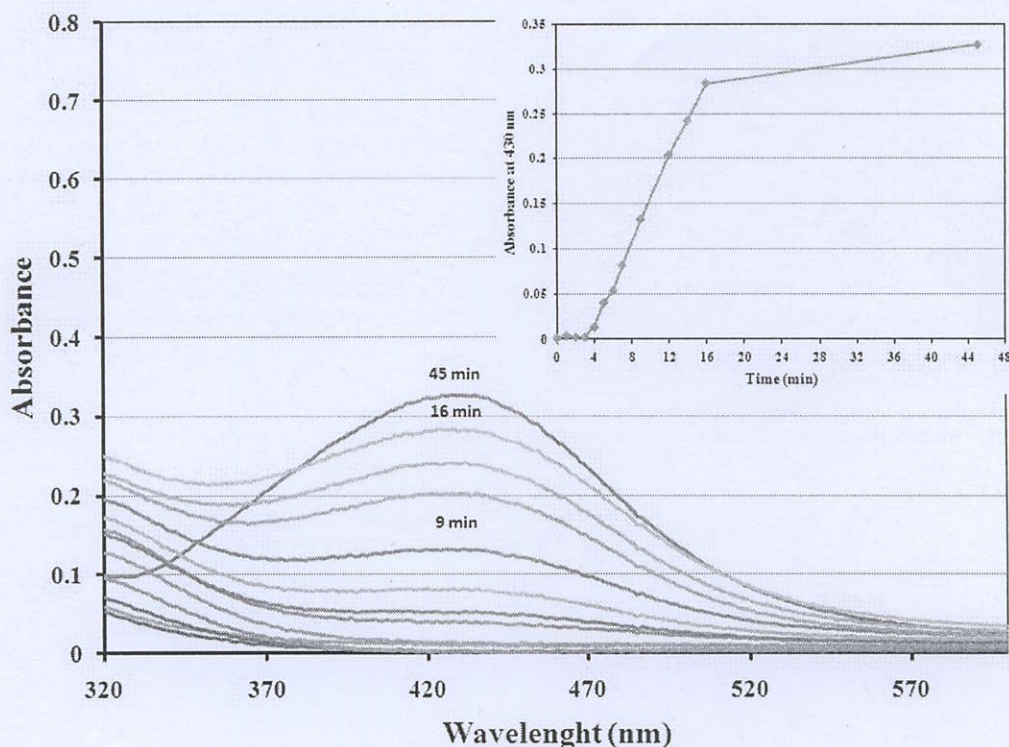


Fig. (1). UV-Vis spectra of HPMo/propan-2-ol/ Ag^+ solution at different stages.

A blank experiment in the absence of UV irradiation revealed that the formation of nanoparticles is very slow and it took place more than six hours.

3.1. Effect of Ag^+ Ions Concentration

It is reported that the size control of Ag NPs can be achieved via the reaction rate control (Equation 4) [26]. Faster reduction of Ag^+ ions leads to smaller and more uniform nanoparticles suggesting that the rate of silver ion reduction affects strongly the initial nucleation of particles. The concentration of silver ions influences the reduction rate which subsequently affects the size of the synthesized particles. This effect was investigated by changing the initial concentration of Ag^+ from 0.25×10^{-4} to 1×10^{-3} M, keeping the initial concentration of HPMo and amount of propan-2-ol constant at 1.75×10^{-6} mol and 2 mL, respectively. The diameters of the synthesized Ag NPs (based on the PSD results) are shown in Fig. (2). As seen in this figure, by decreasing the Ag^+ concentration, smaller and more uniform nanoparticles were produced. Our observation also explained that increasing Ag ions concentration leads to the enhancement of reaction time. In addition, by decreasing the Ag^+ concentration, more stable nanoparticles were obtained. In higher concentrations, a great amount of Ag NPs were deposited after a short time. It might be due to (i) the bigger size of NPs, or (ii) increasing the $[\text{Ag}^+]/[\text{HPMo}]$ ratio in which the amount of HPMo might not be sufficient for Ag NPs stabilization.

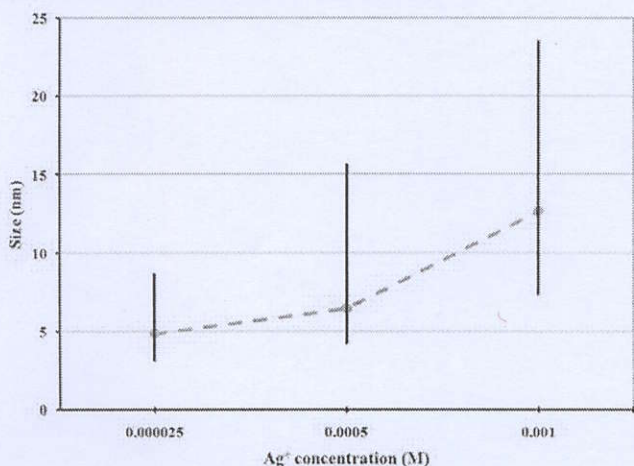


Fig. (2). Effect of initial Ag^+ concentration on size of the synthesized Ag NPs.

It is interesting to note that when the Ag ions concentration was more than 10^{-3} M, Ag NPs was not produced and color of the solution changed from colorless to blue indicating the reduction of HPMo. The differences among the solutions with various Ag^+ concentrations are shown in Fig. (3). As seen in the figure, at Ag^+ concentration of 2×10^{-3} M, there is not any absorption band at 430 nm even after 90 min. This can be explained by the fact that at high concentration of Ag^+ , strong interactions are established between HPMo and Ag^+ . Therefore, Ag^+ is not sufficient in the solution and reduction cannot proceed.

3.2. Effect of Initial dose of HPMo

To find the effect of initial amount of HPMo on the size of Ag NPs produced, the dose of HPMo were changed from 3.28×10^{-7} to 2.8×10^{-6} mol, in which the initial concentration of Ag^+ were kept constant (5×10^{-4} M). In these experiments, controlling the size of Ag NPs was achieved, where the mean diameter of nanoparticles varied between 2.19 and 26.65 nm (see Fig. (4)). As seen in the figure, increasing the initial amount of HPMo from 0.328 to 1.31×10^{-6} mol, results in the formation of smaller NPs in the range

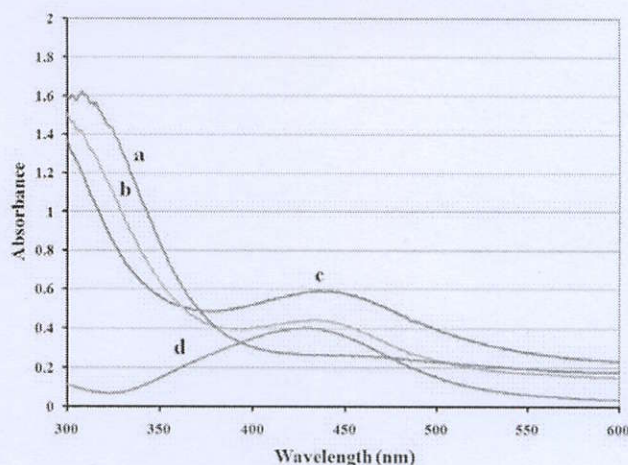


Fig. (3). UV-Vis spectra of Ag NPs colloids with propan-2-ol=2 mL: (a) $[\text{Ag}^+]=2 \times 10^{-3}$ M, $\text{HPMo}=1.75 \times 10^{-6}$ mol; (b) $[\text{Ag}^+]=0.25 \times 10^{-4}$ M, $\text{HPMo}=1.75 \times 10^{-6}$ mol; (c) $[\text{Ag}^+]=0.5 \times 10^{-4}$ M, $\text{HPMo}=1.75 \times 10^{-6}$ mol; (d) $[\text{Ag}^+]=0.5 \times 10^{-4}$ M, $\text{HPMo}=3.28 \times 10^{-7}$ mol.

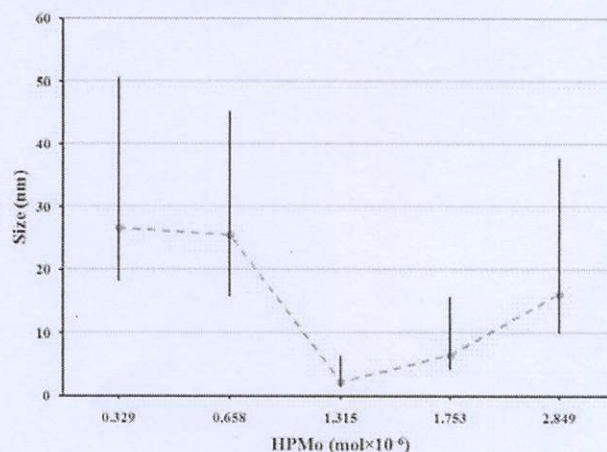


Fig. (4). Effect of HPMo amount on the size of Ag NPs ($[\text{Ag}^+]=5 \times 10^{-4}$ M, propan-2-ol=2 mL).

of 26.65 to 2.19 nm. The fact, in which smaller and more uniform Ag NPs are formed with increasing the initial amount of HPMo, implies that the nucleation process is enhanced more than the growth of these nanoparticles. As an example, the particle size distribution of Ag nanoparticles at 1.31×10^{-6} mol initial value of HPMo is quantitatively displayed in a histogram shown in Fig. (5).

In the HPMo range of 0.328 to 1.31×10^{-6} mol, our findings verify the results of other studies such as Troupis *et al.* [8, 9, 26] and Yang *et al.* [20], in which POMs served as both reducing agents and stabilizers in the synthesis of metal nanoparticles. They have reported that increasing the amount of POM leads to the formation of smaller nanoparticles. Our results show that this is not totally valid for all the initial concentration range of POM. As seen in Fig. (4), increasing the HPMo concentration above 1.31×10^{-6} M, the size of synthesized nanoparticles exhibited a contrary trend. This finding verify the results of our previous study about gold nanoparticles [12, 24] and also Sun *et al.* research regarding platinum nanoparticles [10]. The reason for the opposing trend of large Ag NPs, might be due to higher coverage of HPMo polyanions on the exterior surface of Ag NPs at higher amount of HPMo that reduce the reaction rate in Equation 4. In other words, the concentration of 1.31×10^{-6} M acts as a critical amount of HPMo in the

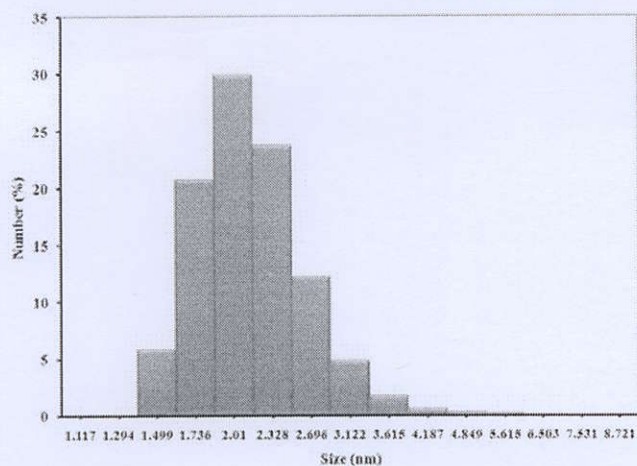


Fig. (5). Particle size distribution of Ag NPs after 15 min irradiation using (HPMo= 1.31×10^{-6} , $[Ag^+] = 5 \times 10^{-4}$ M, propan-2-ol=2 mL).

synthesis of Ag NPs in our experimental conditions. This value depends on the type of metal ions, POM type, propan-2-ol amount and other operating conditions (temp., pH, ionic strength, etc.).

The above finding can be explained by the variation of $[Ag^+]/[HPMo]=\gamma$ molar ratio. Fig. (6) shows the dependency of nanoparticles mean diameter on the γ ratio. As demonstrated in Fig. (6), when γ is less than 3.8, increasing the HPMo amount (decreasing γ ratio) inhibits the reaction progress, thus the growth rate of nanoparticle increases. This behavior is similar to that found in many chemical reduction approaches to nano systems, because the nucleation and growth sequences are both affected by the relative concentrations of both reducing agent and precursor [26]. In our case, we think that in the molar ratio range of less than 3.8, increasing molar ratio the nucleation process overcome the particle growth which results in smaller sized particles. The particle growth becomes faster than the nucleation for the molar ratio higher than 3.8, producing larger nanoparticles.

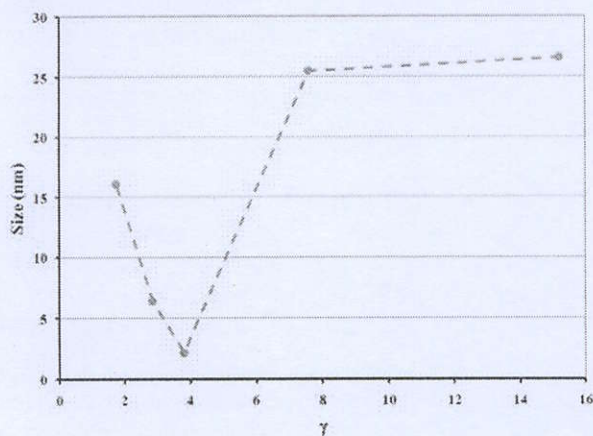


Fig. (6). Effect of $[Ag^+]/[HPMo]$ ratio on the size of Ag NPs ($[Ag^+] = 5 \times 10^{-4}$ M, propan-2-ol=2 mL).

3.3. Effect of Propan-2-ol Amount

In the photolysis of HPMo/propan-2-ol/ Ag^+ solution, the propan-2-ol serves as a sacrificial agent for the photoformation of molybdophosphoric acid, HPMo(e), which further reacts with Ag^+ to produce silver nanoparticles. A control experiment was performed in which 2 mL propan-2-ol was added to 10 mL deaerated aqueous solution of $AgNO_3$ and then irradiated for 6 hours. There was no

change in the color of solution after UV irradiation and the characteristic silver absorption band was not observed. It indicates that the UV-irradiated propan-2-ol is not responsible for the reduction of Ag^+ .

Moreover, it was observed that in the presence of HPMo, when the amount of propan-2-ol was small, there was no change in the color of solution and no Ag NPs were obtained. Also, the amount of propan-2-ol affects the reaction rate and size of the synthesized Ag NPs. As shown in Fig. (7), at constant initial Ag^+ ion concentration (5×10^{-4} M) and HPMo amount (6.6×10^{-7} mol), increasing the propan-2-ol amount, smaller and more uniform nanoparticles were obtained. In fact, increasing the propan-2-ol amount helps nucleation to be faster.

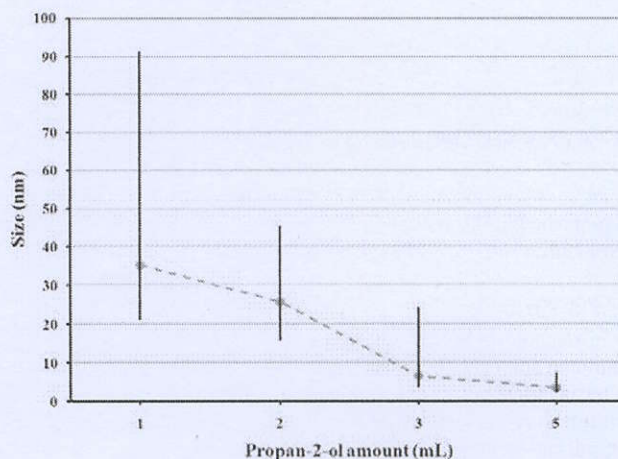


Fig. (7). Effect of propan-2-ol amount on the size of Ag NPs ($[Ag^+] = 5 \times 10^{-4}$ M, HPMo= 6.6×10^{-7} mol).

3.4. Characterization of Ag NPs

In a special condition (Ag^+ concentration= 5×10^{-4} M, HPMo= 6.6×10^{-7} mol, and propan-2-ol=2 mL), the Ag NP products were characterized by TEM. The representative TEM images are shown in Fig. (8). Shapes of the silver nanoparticles are nearly uniform spherical structures. Also, the particle size distribution of these Ag NPs is quantitatively displayed in a histogram shown in Fig. (9). As seen, the particle size distribution indicates that the size of the synthesized Ag NPs varied from about 15.7 nm to 43.8 nm, but most of them have 25.6 nm diameters.

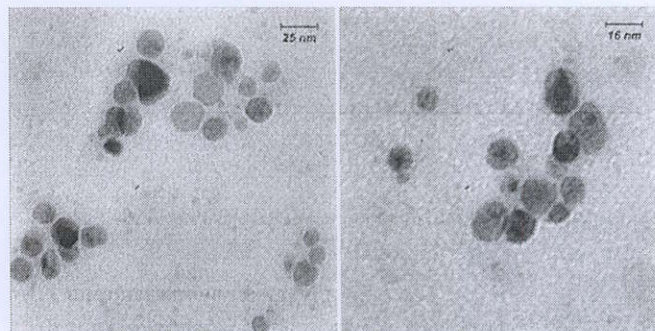


Fig. (8). TEM images of synthesized Ag NPs after 20 min irradiation, $[Ag^+] = 5 \times 10^{-4}$ M, HPMo = 6.6×10^{-7} mol, and propan-2-ol=2 mL.

4. CONCLUSIONS

Molybdophosphoric acid was used as an excellent photocatalyst, reducing agent and stabilizer in the synthesis of silver nanopar-

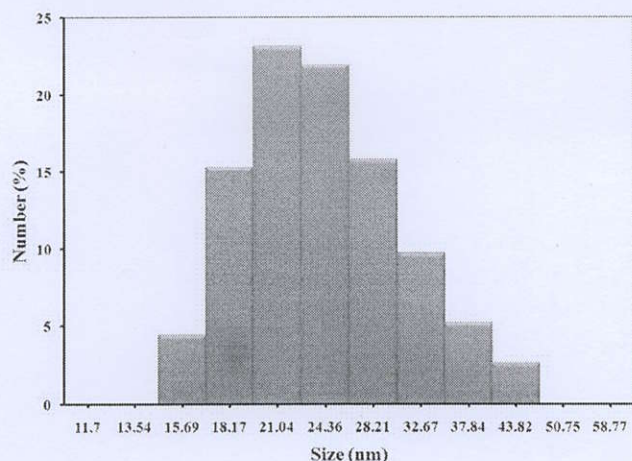


Fig. (9). Particle size distribution of Ag NPs after 20 min irradiation, ($[Ag^+] = 5 \times 10^{-4}$ M, $[HPMo] = 6.6 \times 10^{-7}$ mol, and propan-2-ol=2 mL).

ticles. Uniform and size-controlled Ag NPs were easily prepared by simple photolysis of $HPMo/Ag^+$ /propan-2-ol solution at room temperature. Controlling the size of nanoparticles was achieved by changing the rate of silver reduction via variation of initial Ag ions concentration, molar ratio of silver ions to HPMo, and propan-2-ol amount. Faster reductions result in smaller and more uniform spherical silver nanoparticles, as exhibited by increasing the initial concentration of silver ions or the amount of propan-2-ol. It was found that there is a critical ratio for $[Ag^+]/[HPMo]$ (or dose of initial HPMo), in which in its lower range, increasing the ratio leads to formation of smaller nanoparticles and in its higher value the opposite trend occurs.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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