Application of Molybdophosphoric Acid as Reducing Agent/ Stabilizer in the Synthesis of Gold Nanoparticles under UV Irradiation

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Abstract:
In this paper, we have described the size-controlled synthesis of gold nanoparticles based on the reduction of Au^{3+} ($HAuCl_4$) using molybdophosphoric acid ($H_3[PMo_{12}O_{40}]$, HPMo) under UV-irradiation. In the process, HPMo plays the role of photocatalyst, reducing agent and stabilizer and propan-2-ol acts as a sacrificial agent. This method allows the synthesis of uniform hexagonal nanoparticles with an average size that is tunable between 1.93 and 119 nm by varying the gold ion concentration, HPMo dose (or molar ratio of gold ion to HPMo) and Propan-2-ol amount. We have found that there is a critical ratio for $[Au^{3+}]/[HPMo]$, in which two opposing trends in the size of gold nanoparticles would happened.
Keywords: *Polyoxometalate; Molybdophosphoric acid; Gold; Nanoparticle; UV irradiation.*
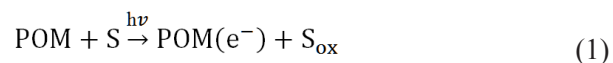
1. INTRODUCTION

In recent years, gold nanostructured materials have attracted great interest due to their intriguing applications in catalysis [1], electronics [2], sensors [3], medicine [4,5], biology [6], etc.. Physical and chemical properties of nanoparticles are the function of size and shape and their applications require non-agglomerated, uniform particles with a controlled mean size and narrow size distribution [7]. Controlling the size of the nanoparticles can be achieved through the control of nucleation and growth steps by changing the synthesis parameters, including the activity of the reducing agents, type and concentration of the precursors, and also nature and amount of protective agents [7,8].

There are several methods such as electrochemical [9], chemical reduction [10, 11], sonochemical [12], photochemical [13], and so on for synthesizing metal nanoparticles. Among them, the chemical reduction of tetrachloroauric acid in the presence of a protecting agent is the most widespread mechanism [14]. However, this conventional approach is based on the use of external chemical reductants that often produce undesirable side products [15]. Therefore, a series of reducing agents has recently been developed for Au-NPs that display a dual role of effective reducing agents of gold ions as well as stabilizers, by providing a robust coating to gold nanoparticles, within a single reaction step [16-19].

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 [20-23]. POMs have unique properties such as: strong Bronsted acidity, high hydrolytic stability (pH=0–12), high thermal stability, operating in pure water without any additive, non-corrosiveness, safety and specially greenness [24, 25]. POM's structures remain unchanged under stepwise and multi-electron redox reactions and can be reduced by photochemical and electrochemical procedures using suitable reducing agents [26, 27].

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. POMs can be reduced in the presence of oxidizable organic substrates (S) like alcohols, under UV irradiation [20]:

$$POM + S \xrightarrow{h\nu} POM(e^-) + S_{ox} \tag{1}$$

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

$$3POM(e^-) + Au^{3+} \rightarrow 3POM + Au^0_{colloid} \tag{2}$$

There are limited reports regarding synthesis of gold nanoparticles (AuNPs) using the above mentioned process. Troupis et al. used the photocatalytic process for AuNPs synthesis in the presence of $H_3[SiW_{12}O_{40}]$ as Keggin type of POM [20]. Also, Mandal et al. have synthesized more complicated nanostructures such as Au–Ag core-shell dimetallic compounds [28] and Au nanosheets [29]. In another study, AuNPs were prepared via this simple photoreduction technique in the presence of transition metal monosubstituted Keggin POMs ($PW_{11}MO_{40}$, M=Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}) [30]. Moreover, in our previous work, we have synthesized AuNPs using Preyssler acid as a green material [31]. Although, the Keggin, mixed-valance and Preyssler types of POMs have been used in the synthesis of Au nanoparticles, but 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 not any report using this type of POM. Furthermore, among the various Keggin type of POMs, HPMo has the highest oxidation potential [32], which can help us synthesize smaller and more uniform nanoparticles.

In the present work, we have investigated, for the first time, the synthesis of AuNPs nanoparticles generated by a simple green chemistry-type process, using HPMo as a photocatalytic reducing agent and stabilizer in the absence of any surfactant or seed at the ambient temperature. Also, the effect of gold ion concentration, dose of HPMo (or molar ratio of gold ion to HPMo) and propan-2-ol amount have also investigated.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

Tetrachloroauric acid, 2-propanol and HPMo were obtained from Merck Company and used as received. UV visible spectra were obtained using Avantes Avaspec-3648 single beam instrument. The synthesized AuNPs were characterized mainly by its particle size distribution using a ZetaSizer Nano ZS apparatus (Malvern Instruments Ltd.) as a laser particle sizer. The instrument helps us determine the particle size by the optoelectronic systems. Also, nanoparticles were characterized using Transmission Electron Microscopy (Philips CM-120).

2.2. AuNPs Synthesis Procedure

In a typical experiment, 5 mL of an aqueous solution of HPMo, 10 mL $HAuCl_4$ and 2 mL propan-2-ol were placed into a spectrophotometer cell and deaerated with N_2 gas. Then, the mixture was irradiated by UV light (125 W high pressure mercury vapor lamp) under continuous stirring. Reaction was performed in a constant room temperature, using water circulating around the cell. The color of the solution changed from yellow to pink, indicating the formation of Au nanoparticles [30]. 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 AuNPs in the reaction between the reduced HPMo ($[PMo_{12}O_{40}]^{4-}$) and Au^{3+} ions. The $[PMo_{12}O_{40}]^{4-}$ ion was obtained by photolysis of a deaerated aqueous solution of propan-2-ol and $(PMo_{12}O_{40})^{3-}$, in which propan-2-ol plays the role of sacrificial agent (equation 1).

After reduction, the color of the solution gradually turned to pink (formation of Au0), due to the ability of reduced HPMo ($[PMo_{12}O_{40}]^{4-}$) for transfering electrons efficiently to gold ions. Equations 1 and 2 were happened in a one-pot system at ambient temperature. Furthermore, HPMo ions can be utilized cyclically as oxidizing or reducing agent according to equations 1 and 2.

The process was monitored by the visible absorption spectrometry. Figure 1 shows the UV/Vis spectra of the mixture of 5mL HPMo ($5.5×10^{-4}$ M), 10 mL $HAuC_{l4}$ ($5×10^{-4}$ M) and 2 mL 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. But, after UV irradiation the absorption bands were observed in the SPR band of gold NPs at about 535 nm. These absorption bands that caused by the excitation of surface-plasmon vibrations, indicate formation of AuNPs. From the figure, it can be observed that the absorption band becomes sharper and the resonance intensity increases due to the increase number of AuNPs during the process. Figure 1 also shows that until 10 min irradiation, there is not any absorption band at 530 nm indicating no nanoparticles was produced. Also, at the first 15 min, the AuNPs production rate (equation 2) is very slow and equation 1 is in progress.

In our previous work, it was shown that in the absence of POMs, particles were precipitated after 2 days [31], but the resulting colloid was stable without any precipitating for several weeks in the presence of HPMo. Even if the precipitation happened, the AuNPs could be easily redispersed by simple hand shaking. These observations indicate the stabilizing role of
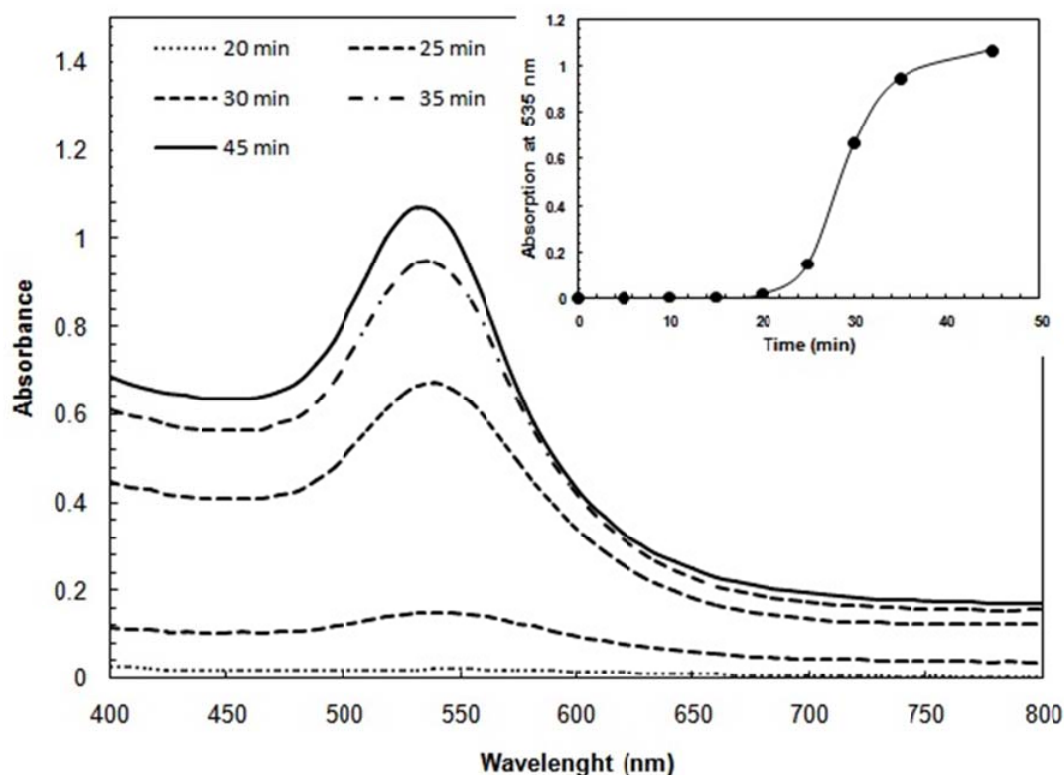

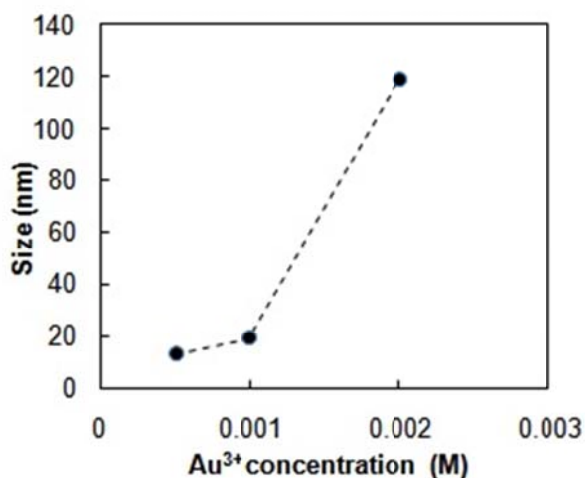**Figure1:** *UV-Vis spectra of HPMo/propan-2-ol/Au³⁺ solution.*

Figure 2: *Effect of initial Au^{3+} concentration on size of the synthesized AuNPs*
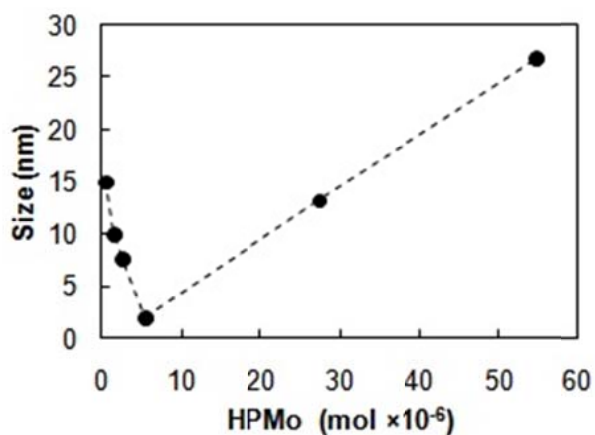

Figure 4: *Effect of $[Au^{3+}]/[HPMo]$ ratio on the size of AuNPs ($[Au^{3+}]=5\times10^{-4}$ M, propan-2-ol=2 mL)*

Figure 3: *Effect of HPMo amount on the size of AuNPs ($[Au^{3+}]=5\times10^{-4}$ M, propan-2-ol=2 mL)*

Figure 5: *Effect of propan-2-ol amount on the size of AuNPs ($[Au^{3+}] = 5\times10^{-4}$ M, HPMo= 2.7×10^{-5} mol)*

HPMo in the mentioned reaction. It might be due to the adsorption of HPMo polyanions onto the surface of AuNPs which provide both kinetic stabilization through coulombic repulsion between the negatively charged particles and also steric stabilization [33]. Therefore, HPMo is an excellent stabilizer to prevent agglomeration. Furthermore, it is easily rinsed after the reaction by washing with water and will not contaminate the nano gold particles.

A blank experiment in the absence of UV irradiation was shown that the formation of nanoparticles is very slow and it took place in more than 8 hours.
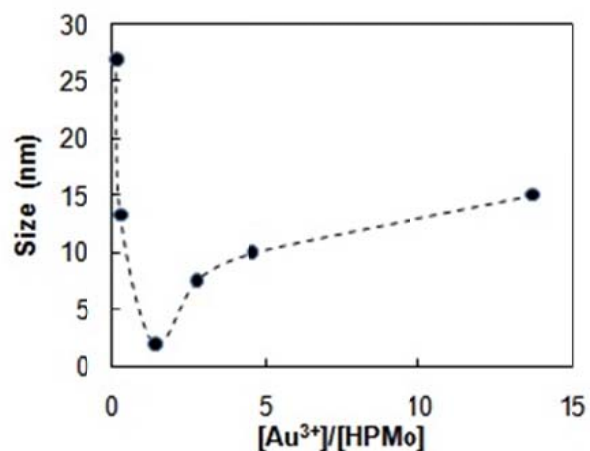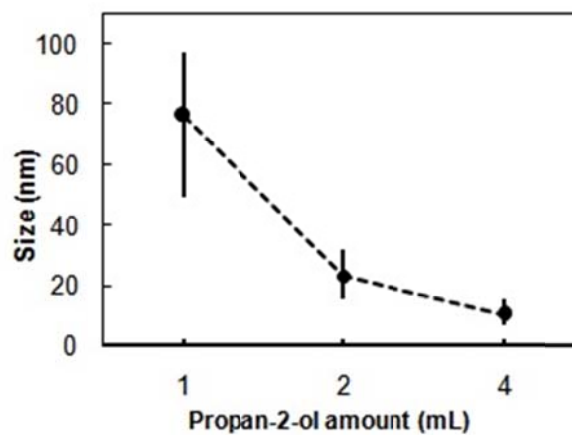
3.1. Effect of Au^{3+} ions concentration

Size control of the nanoparticles can be achieved via rate control of equation 2 [34]. Faster reduction of Au^{3+} ions leads to smaller and more uniform nanoparticles, suggesting that the rate of metal ion reduction strongly affects the initial nucleation of particles. The concentration of metal ions influences the size of the obtained particles. This effect was investigated by changing the initial concentration of Au^{3+} from 5×10^{-4} to 2×10^{-3} M, keeping the initial concentration of HPMo and propan-2-ol amount constant at 2.8×10^{-5} mol and 2 mL, respectively.

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Time of the reaction and average size of the synthesized AuNPs (in the base of PSD results) are shown in Table 1 and Figure 4. As seen in Table 1, by decreasing the Au^{3+} concentration, smaller nanoparticles were produced in shorter time.

Au^{3+} concentration (M)	Time of reaction (min)	Mean diameter of AuNPs (nm)
5×10^{-4}	45	13.25
1×10^{-3}	70	19.62
2×10^{-3}	120	119.17 (not stabilized!)

Moreover, by decreasing the Au^{3+} concentration, more stable nanoparticles were obtained. In higher concentration, a great amount of AuNPs were deposited after a short time. It might be due to (i) their bigger size, or (ii) increasing $[Au^{3+}]/[HPMo]$ ratio in which the amount of HPMo might not be sufficient for AuNPs stabilization.

3.2. Effect of initial dose of HPMo or molar ratio of gold ions to HPMo

To find the effect of initial amount of HPMo on the size of AuNPs produced, the dose of HPMo were changed from 5×10^{-7} to 55×10^{-6}, in which the initial concentration of Au^{3+} were kept constant (5×10^{-4} M). In these experiments, the size of AuNPs tried to be controlled and as can be seen in Figure 3, the mean diameters of nanoparticles were decreased from 26.9 to 1.93 nm. It was observed that increasing the initial amount of HPMo from 0.55 to 5.5×10^{-6} mol, results in the formation of smaller nanoparticles in the range of 15 to 1.93 nm. The fact in which smaller AuNPs are formed with increasing the initial amount of HPMo implies that the nucleation process is enhanced more than the growth of these nanoparticles.

In the HPMo concentration range of 0.55 to 5.5×10^{-6} mol, our findings verify the results of other studies such as Troupis *et al.* [21, 20, 34] and Yang *et al.* [35] in which POM served as both reducing agents and stabilizers in the synthesis of metal nanoparticles. They have reported that increasing the POM amount leads to the formation of smaller nanoparticles. But, our results show that this is not true in all the initial concentration range of POM. As seen in Figure 3, by increasing the HPMo concentration above 5.5×10^{-6} M, the size of the synthesized nanoparticles exhibited a contrary trend. This findings verify the results of our previous study [31] and also sun et al. research [33]. The reason for the opposing trend of large AuNPs, might be due to higher coverage of HPMo polyanions on the exterior surface of AuNPs at higher amount of HPMo that reduce the reaction rate in equation 2.

In another word, the concentration of 5.5×10^{-6} M acts as a critical amount of HPMo in the synthesis of AuNPs in our experimental condition. This value
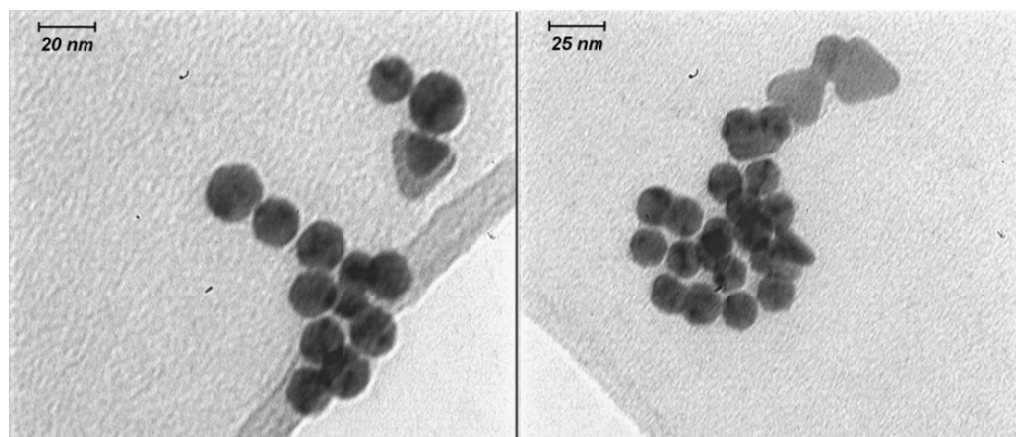

Figure 6: *TEM images of synthesized AuNPs after 35 min irradiation ($[Au^{3+}]=5\times10^{-4}$ M, HPMo=5.5 $\times10^{-7}$ mol, and propan-2-ol=2 mL).*

depends on the type of metal ions, POM type, and other operating conditions (temp., pH, ionic strength, etc.).

Figure 4 shows the dependency of nanoparticles diameter on the molar ratios of Au^{3+} ion to HPMo. As demonstrated in Figure 4, when molar ratio of Au^{3+} ion to HPMo is less than 1.36, increasing the HPMo amount inhibits the reaction progress, so 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 the reducing agent and the precursor [34]. In our case, we think that in the range of molar ratio less than 1.36, by increasing the molar ratio the nucleation process is overwhelmingly faster than particle growth which results in smaller sized particles. The particle growth becomes faster than the nucleation for the molar ratio bigger than 1.36, producing larger nanoparticles.

3.3. Effect of Propan-2-ol amount

In the photolysis of HPMo/propan-2-ol/Au^{3+} solution, the propan-2-ol serves as a sacrificial agent for the photoformation of molybdophosphoric acid, HPMo(e-), which further reacts with Au^{3+} to produce gold nanoparticles. A control experiment was perf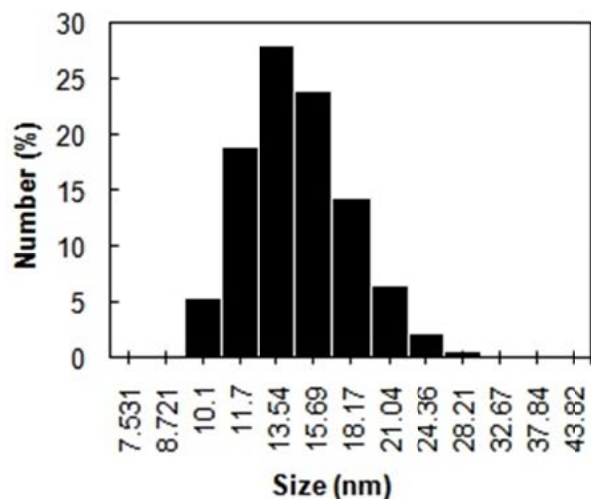ormed in which 2 mL prpan-2-ol and 10 mL was added to deaerated aqueous solution of $HAuC_{l4}$ and irradiated for 6 hours. There was no change in color of the solution after UV irradiation and the characteristic gold absorption band was not observed. It indicates that the product of UV-irradiated prpan-2-ol is not responsible for the reduction of Au^{3+}.

It was observed that when the amount of propan-2-ol was less than 0.6 mL, there was not any color change and no gold NPs were obtained. Also, the amount of propan-2-ol affects the reaction rate and size of the synthesized AuNPs. As shown in Figure 5, at constant initial Au^{3+} ion concentration (5×10^{-4} M) and HPMo amount (2.7×10^{-5} mol), by increasing the propan-2-ol, smaller and more uniform nanoparticles were obtained. In fact, increasing the propan-2-ol amount helps nucleation to be faster.

3.4. Characterization of AuNPs

In a special condition (Au^{3+} concentration=5×10^{-4} M, HPMo=5.5×10^{-7} mol, and propan-2-ol=2 mL), the AuNP products were characterized by TEM. The representative TEM images are shown in Figure 6. The shapes of the gold nanoparticles are nearly uniform hexagonal structures. Also, the particle size distribution of these AuNPs is quantitatively displayed in a histogram shown in Figure 7. As seen, the particle size distribution indicates that size of the synthesized AuNPs varied from about 10 nm to 32.67 nm, but 15 nm diameters were the most abundant.

4. CONCLUSIONS

Molybdophosphoric acid was used as an excellent photocatalyst, reducing agent and stabilizer in the synthesis of gold nanoparticles. Uniform, size-controlled gold nanoparticles were easily prepared by simple photolysis of HPMo/Au^{3+}/propan-2-ol solution at room temperature. Controlling the size of nanoparticles was achieved by changing the rate of gold reduction via variation of initial gold ions concentration, molar ratio of gold ions to HPMo, and prpan-2-ol amount. Faster reductions result in smaller and more uniform hexagonal gold nanoparticles as exhibited by increasing the

Figure 7: *Particle size distribution of AuNPs after 35 min UV irradiation ([Au^{3+}]=5×10^{-4} M, HPMo=5.5×10^{-7} mol, and propan-2-ol=2 mL)*

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initial concentration of gold ions or the propan-2-ol amount. It was found that there is a critical ratio for $[Au^{3+}]/[HPMo]$ (or dose of initial HPMo), in which for its lower range, increasing the ratio leads to the formation of smaller nanoparticles and in its higher value the opposite trend is happened.

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