

Size-controlled and Green Synthesis of Metal Nanoparticles Using Molybdophosphoric Acid

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Abstract: Green synthesis of silver and gold nanoparticles as two metal nanoparticles, was studied based on photoreduction of metal ions using molybdophosphoric acid ($H_3[PMo_{12}O_{40}]$, HPMo) under UV-irradiation. HPMo was found to be photocatalyst, reducing agent and efficient stabilizer for the resulting nanoparticles. This method allows the size-controlled synthesis of uniform nanoparticles with an average size that is tunable by varying the initial used HPMo amount. We have found that there is a critical value for HPMo amount, in which two opposing trends in the size of metal nanoparticles would happen. This value is depends on the type of metal and reaction conditions and for Au NPs it is higher than that of Ag NPs.

Key-Words: Metal; Nanoparticle; Polyoxometalate; Molybdophosphoric acid; UV irradiation.

1 Introduction

Metal nanostructured materials are intriguing interest due to their variety applications in catalysis, electronics, sensors, medicine, etc.[1, 2]. Several methods have been reported for synthesis of the metal nanoparticles (NPs) such as electrochemical [2], chemical reduction [3], sonochemical [4], photochemical [5], and so on using various reagents. Among all preparation methods, the chemical reduction of metal ions in the presence of a protecting agent is the most widespread way [6]. Based on the green chemistry principles, the green synthesis of Ag NPs involves selection of an ecofriendly solvent and environmentally benign reducing agent [7]. In this basis, most of the employed reductants are opposing green chemistry and most of the reactions were performed at high temperature.

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, 9]. 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 and safety [10, 11]. POM's structures remain unchanged under stepwise and multielectron redox reactions and can be reduced by photochemical and electrochemical

procedures using suitable reducing agents [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.

There are limited reports regarding synthesis of metal NPs using POMs [9]. Troupis et al. used the photocatalytic process for Au, Ag, Ni, Pt NPs synthesis in the presence of $H_3[SiW_{12}O_{40}]$ as Keggin type of POM [8]. Also, Mandal et al. have synthesized more complicated nanostructures such as Au–Ag core-shell dimetallic compounds [13] and Au nanosheets [14]. In another study, Au NPs 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+}) [15]. Moreover, in our previous works, we have synthesized Au and Ag NPs using Preyssler acid in two different processes [16, 17]. Although, the Keggin, mixed-valance and Preyssler types of POMs have been used in the synthesis of metal NPs, but in the base of our knowledge, the role of molybdophosphoric acid ($H_3[PMO_{12}O_{40}]$, HPMo) has been largely overlooked. Furthermore, among the various Keggin type of POMs, HPMo has the highest oxidation potential [18], which can help to

synthesis smaller and more uniform NPs.

In the present work we have used Molybdophosphoric acid as photocatalytic reducing agent and stabilizer to synthesis metal nanoparticles via a green, simple and efficient photoreduction technique at ambient temperature. Besides, HPMo concentration has also investigated.

2 Experimental

2.1 Chemicals and Apparatus

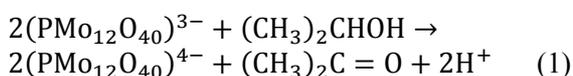
All the chemicals were obtained from Merck Company and used as received. UV visible spectra were obtained using Avantes Avaspec-3648 single beam instrument. The synthesized metal NPs were characterized mainly by its particle size distribution using a ZetaSizer Nano ZS apparatus (Malvern Instruments Ltd.) as a laser particle sizer. Also, nanoparticles were characterized using Transmission Electron Microscopy (Philips CM-120).

2.2 Facile metal NPs Synthesis Procedure

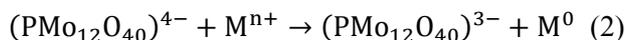
In a typical experiment, 5 mL of an aqueous solution of HPMo, 10 mL metal ions and 2 mL propan-2-ol were placed into a spectrophotometer cell and deaerated with N₂ gas for 15 min. Then, the mixture was irradiated by UV light (125 W high pressure mercury vapour lamp) under continuous stirring. Reaction was performed in a constant room temperature, using water circulating around the cell. Changing the colour of solution from colourless to yellow (Ag NPs) or pink (Au NPs) indicated the formation of corresponding nanoparticles. The nanoparticles can be separated by a high speed centrifuge (14000 rpm), and washed twice with water.

3 Results and Discussion

HPMo was chosen to study the synthesis of Ag NPs in a reaction between the reduced HPMo ([PMo₁₂O₄₀]⁴⁻) and Ag⁺ ions. The [PMo₁₂O₄₀]⁴⁻ ion was obtained by photolysis of a deaerated aqueous solution of propan-2-ol and (PMo₁₂O₄₀)³⁻, in which propan-2-ol plays the role of sacrificial agent (Equation 1).



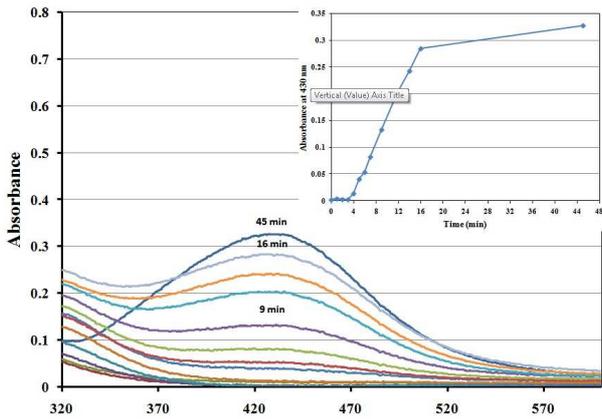
After reduction, the colour of the solution changed gradually, due to the ability of [PMo₁₂O₄₀]⁴⁻ for transferring electrons efficiently to metal ions.



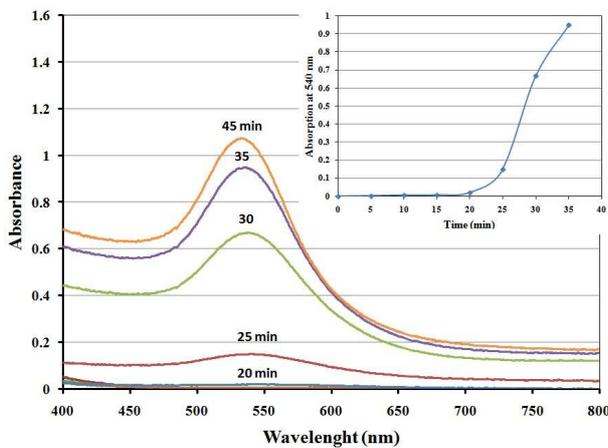
These two equations were occurred in a one-pot system at ambient temperature. HPMo ions can be utilized cyclically as oxidizing or reducing agent according to equations 1 and 2. The process was monitored by the visible absorption spectrometry. Figure 1 shows the UV/Vis spectra of the mixtures for the synthesis of gold and silver nanoparticles, 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 and in the SPR band of silver at 430 nm. These absorption bands that caused by the excitation of surface-plasmon vibrations, indicate formation of Au and Ag NPs. From the figure, it can be observed that the absorption band becomes sharper and the resonance intensity increases due to the increase number of metal NPs during the process. Figure 1 also shows that until 10 min irradiation for silver and until 20 min for gold, there is not any absorption band at 430 and 530 nm indicating no nanoparticles was produced. In these intervals, the metal nanoparticles production rate (equation 2) is very slow and equation 1 is in progress. Also, this figure shows that the rate of nanoparticles synthesis strongly depends on kind of metal ions. As seen, Ag NPs prepares rapidly, faster than Au NPs.

Usually, the synthesized nanoparticles were apt to aggregate and precipitate in the solution due to coulomb or van der Waals forces. It was indicated that in the absence of POMs, particles were precipitated after a few days [16], but the resulting colloid was stable without any precipitating for several months in the presence of HPMo. These observations indicate the stabilizing role of HPMo in the mentioned reaction. It might be due to the adsorption of HPMo polyanions onto the surface of nanoparticles which provide both kinetic stabilization through coulombic repulsion between the negatively charged particles and also steric stabilization [19]. Therefore, HPMo is an excellent stabilizer to prevent agglomeration. Also, it is easily rinsed after the reaction by washing with water and will not contaminate the nanoparticles.



(a)



(b)

Figure 1. UV-Vis spectra of (a) HPMo (1.3×10^{-4} M)/propan-2-ol (2 mL)/Ag⁺ (5×10^{-4} M), (b) HPMo (5.5×10^{-4} M)/propan-2-ol (2 mL)/Au³⁺ (5×10^{-4} M) solution at different stages.

In the photolysis of HPMo/propan-2-ol/ M^{n+} solution, the propan-2-ol serves as a sacrificial agent for the photoformation of molybdophosphoric acid, HPMo(e⁻), which further reacts with M^{n+} to produce metal nanoparticles. A control experiment was performed in which 2 mL propan-2-ol and 10 mL was added to deaerated aqueous solution of metal ions and irradiated for 6 hours. There was no change in colour of the solution after UV irradiation and the characteristic absorption bands were not observed. It indicates that the product of UV-irradiated propan-2-ol is not responsible for the reduction of M^{n+} . The synthesized silver and gold nanoparticles were characterized by TEM and PSD. The representative TEM images and PSD histograms of nanoparticles are shown in Figures 2 and 3. The shapes of both kinds of nanoparticle are nearly uniform spherical structures. Also, the particle size distributions indicate that Au NPs (mean diameter about 15 nm)

are smaller and more uniform than Ag NPs (mean diameter about 26 nm).

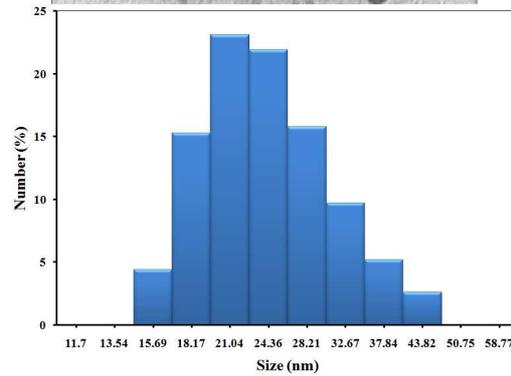
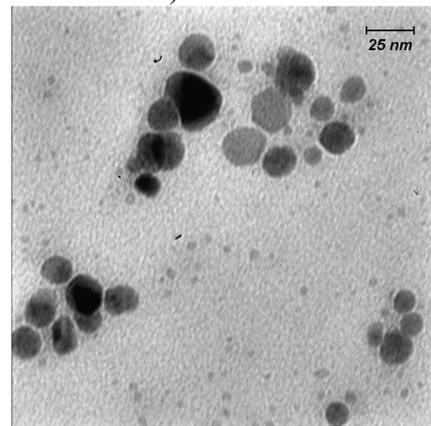


Figure 2. TEM image and PSD histograms of synthesized Ag NPs.

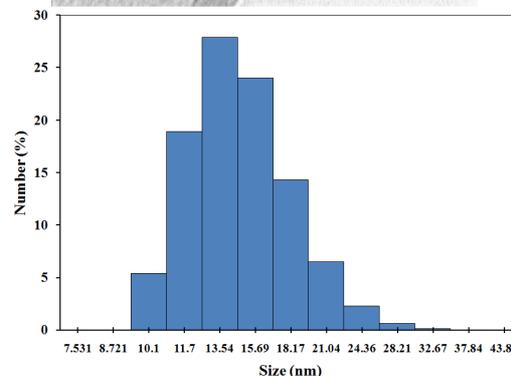
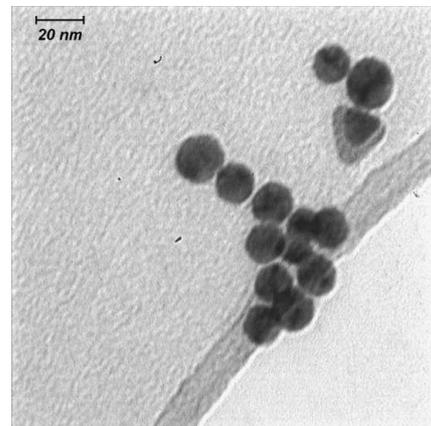


Figure 3. TEM image and PSD histograms of synthesized Au NPs.

To find the effect of initial amount of HPMo on the size of metal NPs produced, the dose of HPMo were changed from 5×10^{-7} to 55×10^{-6} for Au NPs and from 3.28×10^{-7} to 2.8×10^{-6} for Ag NPs, in which the initial concentration of metal ions were kept constant at 5×10^{-4} M. The results are shown in Figures 4 and 5 for Ag and Au NPs synthesis, respectively. In these experiments, controlling the size of metal NPs was achieved by changing the HPMo amount (as shown in Figures 4 and 5). As seen in the figures, in low HPMo concentration, increasing the initial amount of HPMo results in the formation of smaller nanoparticles. Our observations represent that in this range, the rate of reaction increases by increasing of HPMo amount. The fact in which smaller metal nanoparticles are formed with increasing the initial amount of HPMo implies that the nucleation process is enhanced more than the growth of these nanoparticles.

But, our results show that this is not true in all the initial concentration range of HPMo. As seen in Figures 4 and 5, increasing the HPMo concentration above 5.5×10^{-6} mol for Au NPs and 1.31×10^{-6} mol for Ag NPs, the size of the synthesized nanoparticles exhibited a contrary trend. The reason for the opposing trend of large metal nanoparticles, might be due to higher coverage of HPMo polyanions on the exterior surface of nanoparticles at higher amount of HPMo that reduce the reaction rate in equation 2.

In another word, the dose of 5.5×10^{-6} and 1.31×10^{-6} act as critical amounts of HPMo in the synthesis of Au NPs and Ag NPs in our experimental condition. As seen, this value depends on the type of metal ions. Also, it depends on POM type, and other operating conditions (temp., pH, ionic strength, etc.).

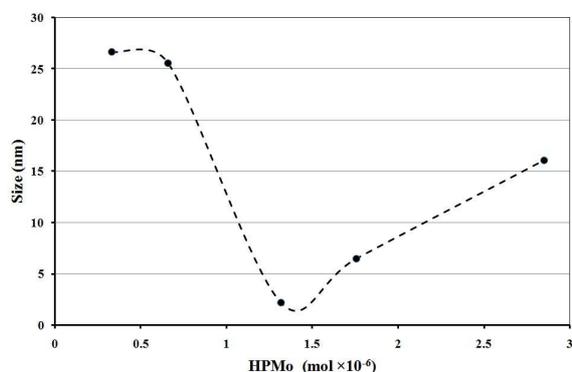


Figure 4. Effect of HPMo amount on the size of Ag NPs ($[Ag^+] = 5 \times 10^{-4}$ M, propan-2-ol=2 mL).

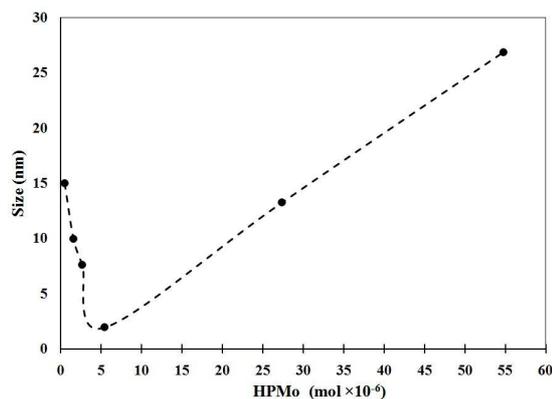


Figure 5. Effect of HPMo amount on the size of Au NPs ($[A^{3+}] = 5 \times 10^{-4}$ M, propan-2-ol=2 mL).

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/Au³⁺/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 HPMo amount. Faster reductions result in smaller and more uniform metal nanoparticles. It was found that there is a critical value for 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. This value for gold is 5.5×10^{-6} mol, which is higher than that for Ag NPs (1.31×10^{-6})

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