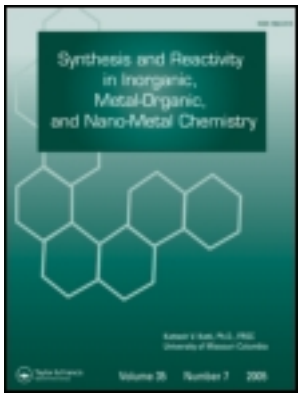

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

A Green and Simple Route for the Controlled-Size Synthesis of Gold Nanoparticles Using Preyssler Heteropolyacid

Ali Ayati [a] , Ali Ahmadpour [a] , Fatemeh F. Bamoharram [b] & Majid M. Heravi [c]

[a] Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, I. R. I. R. Iran

[b] Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, I. R. Iran

[c] Department of Chemistry, School of Sciences, Alzahra University, Tehran, I. R. Iran

Accepted author version posted online: 14 Aug 2012.Version of record first published: 01 Oct 2012.

To cite this article: Ali Ayati , Ali Ahmadpour , Fatemeh F. Bamoharram & Majid M. Heravi (2012): A Green and Simple Route for the Controlled-Size Synthesis of Gold Nanoparticles Using Preyssler Heteropolyacid, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:9, 1309-1314

To link to this article: http://dx.doi.org/10.1080/15533174.2012.684255

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:1309–1314, 2012

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.684255

Taylor & Francis
Taylor & Francis Group

A Green and Simple Route for the Controlled-Size Synthesis of Gold Nanoparticles Using Preyssler Heteropolyacid

Ali Ayati,[1] Ali Ahmadpour,[1] Fatemeh F. Bamoharram,[2] and Majid M. Heravi[3]

[1]*Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, I. R. I. R. Iran*
[2]*Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, I. R. Iran*
[3]*Department of Chemistry, School of Sciences, Alzahra University, Tehran, I. R. Iran*

The authors describe a facile procedure for size-controlled synthesis of gold nanoparticles based on the reduction of Au^{3+} ($HAuCl_4$) using Preyssler heteropolyacid ($H_{14}[NaP_5W_{30}O_{110}]$) under UV irradiation. Preyssler plays the role of green reducing agent and also efficient stabilizer. This method allows the synthesis of uniform hexagonal nanoparticles with an average size that is tunable between 1.35 and 86.7 nm by varying the gold ion concentration, molar ratio of gold ion to Preyssler, and Propan-2-ol amount. The authors found that there is a critical ratio for [Au^{3+}]/[Preyssler] in which two opposing trends in the size of nanoparticles would happened.

Keywords gold, green synthesis, nanoparticle, polyoxometalate, Preyssler

INTRODUCTION

In recent years, gold nanoparticles (Au NPs) are intriguing interest due to their variety applications in catalysis, electronics, sensors, and medicine.[1,2] There are several methods for the synthesis of these nanoparticles, such as electrochemical,[2] chemical reduction,[3] sonochemical,[4] and photochemical.[5] To date, solution-based wet chemical synthesis is believed to be the best route to new nanostructures, although use of an organic environment and relatively high temperature are common in most of these procedures.

Based on the green chemistry principles, the green synthesis of nanoparticles involves selection of an eco-friendly solvent and environmentally benign reducing agent.[6] In this basis, most of the employed reductants in the synthesis of Au NPs are opposing 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.[7–10] 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 aspects of solid POMs are related to their green synthesis in an aqueous process and achievements of successful practical applications.

The applications of POM compounds have attracted much attention particularly in the last two decades.[11] They posses intriguing structure and diverse properties such as: strong Bronsted acidity, high hydrolytic stability (pH = 0–12), high thermal stability, and operating in pure water without any additive.[12,13] Their structures remain unchanged under stepwise and multielectron redox reactions and these compounds can be reduced by electrochemical and photochemical procedures using suitable reducing agents.[14,15] These properties encourage researchers to use them in the synthesis of metal nanoparticles using simple and efficient methods in an ambient temperature.[16,17]

There are limited reports describing the synthesis of Au nanoparticles using POMs.[8,18–20] Troupis et al. demonstrated that Keggin heteropolyanions $[SiW_{12}O_{40}]^{5-}$ and $[PW_{12}O_{40}]^{4-}$ can be used as photocatalysts, mild reductants, and stabilizers for the synthesis of metal nanoparticles such as Ag, Au, Pt, and Pd upon illumination with UV/near-vis light.[8,18] They have shown POMs can be reduced in the presence of oxidizable organic substrates (S) such as alcohols under UV irradiation:

$$\mathrm{POM} + \mathrm{S} \xrightarrow{h\nu} \mathrm{POM}(\mathrm{e}^-) + \mathrm{S}_{\mathrm{ox}} \qquad [1]$$

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

$$3\mathrm{POM}(\mathrm{e}^-) + \mathrm{Au}^{3+} \rightarrow 3\mathrm{POM} + \mathrm{Au}^0_{\mathrm{colloid}} \qquad [2]$$

Also, Mandal et al. synthesized more complicated nanostructures such as Au–Ag core-shell dimetallic compounds[19] and Au nanosheets.[21] In another study, Au nanoparticles were prepared via a simple photoreduction technique in the presence of transition metal monosubstituted Keggin heteropolyanions

Received 21 September 2011; accepted 8 April 2012.
Address correspondence to A. Ahmadpour, Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, I. R. I. R. Iran. E-mail: ahmadpour@um.ac.ir

($PW_{11}MO_{40}$, M = Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}) as reducing agent, photocatalyst, and stabilizer.[20]

We have found that among all different POMs, the Preyssler structure has an excellent activity in the synthesis of Au NPs as a reducing agent and stabilizer.[22] This kind of POM is remarkable because of the following characteristics: (a) strong Bronsted acidity with 14 acidic protons, (b) reusability, and (c) high oxidation potential, besides the other mentioned advantages.[23]

In continuation of our recent work in the area of nanoscience regarding synthesis and application of POMs,[10,17,22–25] in the present work we used Preyssler acid in the synthesis of gold nanoparticles as a green reducing agent and stabilizer via a simple photoreduction technique at ambient temperature. Besides, the effect of Au^{3+} ion concentration, initial amount of Preyssler acid (or molar ratio of gold ion to Preyssler acid) and propan-2-ol amount have also investigated.

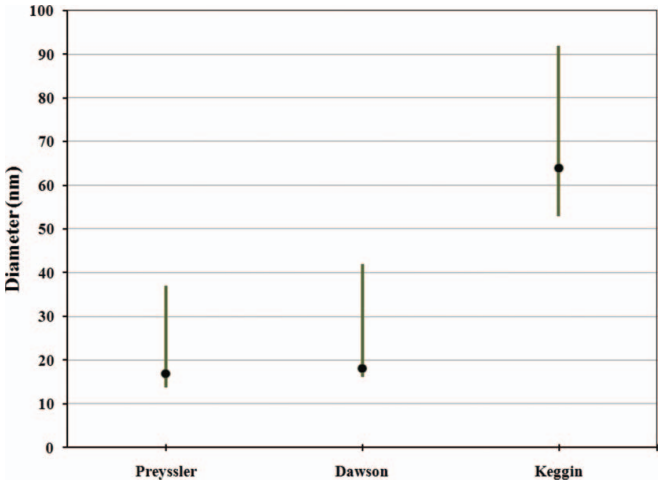

FIG. 1. Effect of POM structures on the Au NPs size after 45 min irradiation ($[HAuCl_4] = 10^{-3}$ M)[22] (color figure available online).

EXPERIMENTAL

Chemicals and Apparatus

$HAuCl_4.3H_2O$, $H_3PW_{12}O_{40}$ and propan-2-ol (analytical grade, extra pure) were obtained from Merck Company (Germany) and used as received. $H_{14}[NaP_5W_{30}O_{110}]$ and $H_6P_2W_{18}O_{62}$ were prepared according to our earlier works.[26,27]

UV-visible spectra were obtained using Avantes Avaspec-3648 single beam instrument (the Netherlands). The synthesized Au NPs were characterized mainly by theirs particle size distribution using a ZetaSizer Nano ZS apparatus (Malvern Instruments Ltd., Worcestershire, UK) as a laser particle sizer. The instrument allowed the measurement of the particle size taking the advantage of optoelectronic systems. Also, nanoparticles were characterized using transmission electron microscopy (Philips CM-120, Hillsborg, USA).

Au NPs Synthesis Procedure

In a typical experiment, 5 mL of an aqueous solution of Preyssler acid, 10 mL $HAuCl_4$, and 2 mL propan-2-ol were placed into a spectrophotometer cell and dearated with N_2 gas. Then, the mixture was irradiated by UV light (125 W high-pressure mercury vapor lamp) under continuous stirring. The temperature of reaction was kept constant at room temperature using water circulating around the cell. The color of the solution changed from colorless to pink, indicating the formation of Au nanoparticles. The nanoparticles were separated by a high-speed centrifuge (14000 rpm) and then washed twice with water. In the washing stage, Preyssler is dissolved in the water and only Au NPs remain. The time of reaction was fixed at 45 min.

RESULTS AND DISCUSSION

In our recent study, we have found that Preyssler acid could be used as an excellent reducing agent and stabilizer in the synthesis of Au NPs.[22] Among the three commonly used POM structures namely Keggin ($H_3PW_{12}O_{40}$), Dawson ($H_6P_2W_{18}O_{62}$), and Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$), the latter has shown highest activity and the resulting particles were smaller and more uniform (see Figure 1).

Therefore, Preyssler acid was chosen to study the synthesis of Au NPs in the reaction between the reduced Preyssler ($[NaP_5W_{30}O_{110}]^{15-}$) and Au^{3+} ions. The $[NaP_5W_{30}O_{110}]^{15-}$ ion was obtained by photolysis of a dearated aqueous solution of propan-2-ol and $[NaP_5W_{30}O_{110}]^{14-}$, in which propan-2-ol plays the role of sacrificial agent (Eqs. 1 and 2).

After reduction, the color of the solution turned gradually to pink (formation of Au^0), due to the ability of reduced Preyssler ($[NaP_5W_{30}O_{110}]^{15-}$) for transferring electrons efficiently to gold ions. Equations 1 and 2 were happened in a one-pot system at ambient temperature. Furthermore, Preyssler ions can be utilized cyclically as oxidizing or reducing agent. In the absence of UV irradiation and also in the absence of Preyssler acid, formation of Au NPs is very slow.

The process was monitored by the visible absorption spectrometry. Figure 2 shows the UV/vis spectra of the mixture of 5 mL Preyssler acid (6.7×10^{-7} M), 10 mL $HAuCl_4$ (10^{-3} 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 400–650 nm. But, after UV irradiation the absorption bands were observed in the SPR band of Au NPs at about 540 nm. These absorption bands that caused by the excitation of surface-plasmon vibrations, indicate formation of Au 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 Au NPs during the process. The reaction progress is shown in Figure 2. As seen in this figure, until 15 min irradiation, there is not any absorption band at 540 nm indicating no formation of nanoparticle. Also, at this

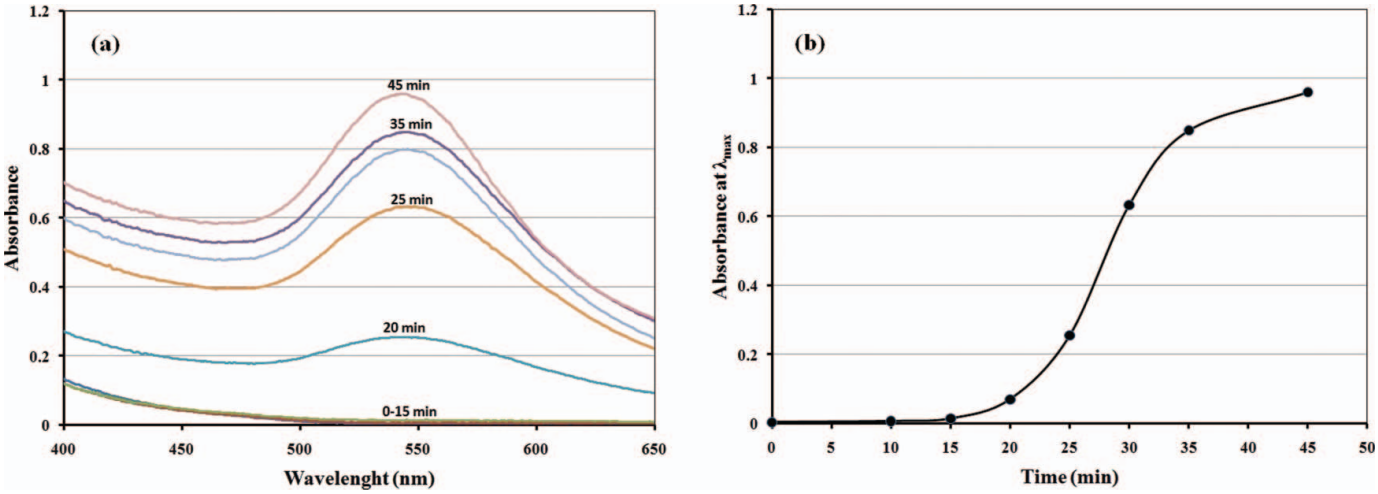

FIG. 2. (a) UV-vis spectra of Preyssler/propan-2-ol/Au^{3+} solution at different stages. (b) Au NP synthesis reaction progress (color figure available online).

time interval, the Au NPs production rate (Eq. 2) is negligible and Eq. 1 is in progress.

Preyssler acid acts as an excellent stabilizer to prevent agglomeration of Au NPs and adsorption of Preyssler polyanions onto the surface of Au NPs leads to inhibition of NPs precipitation for a long time.

Effect of Au^{3+} Ions Concentration

Controlling the size of Au NPs can be achieved via rate control of Eq. 2.[16] Faster reduction of Au^{3+} ions leads to smaller and more uniform nanoparticles suggesting that the rate of metal ion reduction affects strongly the initial nucleation of particles. In the synthesis of Au NPs, the concentration of gold ions is a parameter that influences the rate of reaction and size of the obtained particles. This effect was investigated by changing the initial concentration of Au^{3+} from 10^{-4} to 5×10^{-3} M, keeping the initial concentration of Preyssler and propan-2-ol amount constant at 4×10^{-6} mol and 2 mL, respectively.

Figure 3 shows the relation between Au^{3+} concentration and mean diameters of the synthesized NPs (based on the PSD results). As seen, by decreasing the Au^{3+} concentration, smaller NPs were produced. In our previous study regarding synthesis of Au NPs using molybdophosphoric acid,[24] we showed that increasing Au ions concentration leads to increase of reaction time. In addition, by decreasing the Au^{3+} concentration, more stable nanoparticles were obtained. Our observations have shown that, when the Au^{3+} concentration is $\geq 5 \times 10^{-3}$, the prepared Au NPs precipitate after a day, but for Au^{3+} concentration in the order of 10^{-4}, the NPs are stable for more than 3 months. In higher concentrations, a great amount of Au NPs were deposited after a short time. It might be due to the bigger size of NPs or increasing the $[Au^{3+}]$/[Preyssler] ratio in which the amount of Preyssler might not be sufficient for Au NPs stabilization.

Effect of Initial Preyssler Acid Concentration

Au NPs were synthesized using very little amount of Preyssler acid. The initial amount of Preyssler is the most effective parameter that affects the reaction rate and consequently the size of prepared Au NPs. To investigate the effect of this parameter on the size of Au NPs, the dose of Preyssler were changed from 1.3×10^{-7} to 4×10^{-6}, in which the initial concentration of Au^{3+} were kept constant (10^{-3} M). In these experiments, controlling the size of Au NPs was achieved, where the mean diameter of nanoparticles varied between 1.35 and 47.8 nm (as shown in Figure 4). As seen in the figure, increasing the initial amount of Preyssler from 1.3 to 6.6×10^{-7} mol, results in decreasing the size of nanoparticles (from 15 to 1.93 nm).

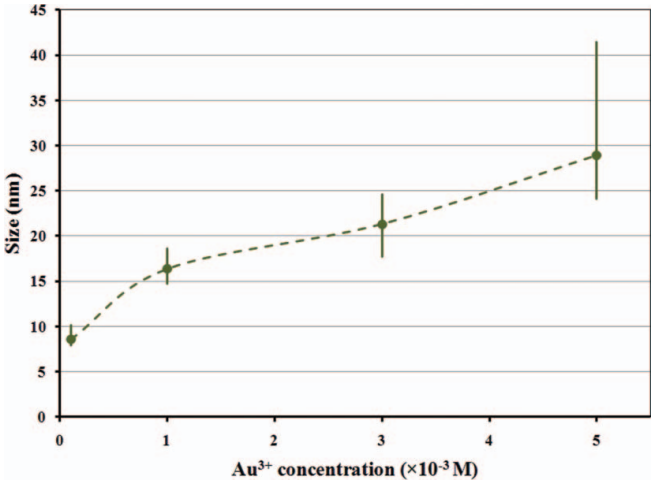

FIG. 3. Effect of initial Au^{3+} concentration on the size of synthesized Au NPs (Preyssler = 4×10^{-6} mol) after 45-min irradiation (color figure available online).

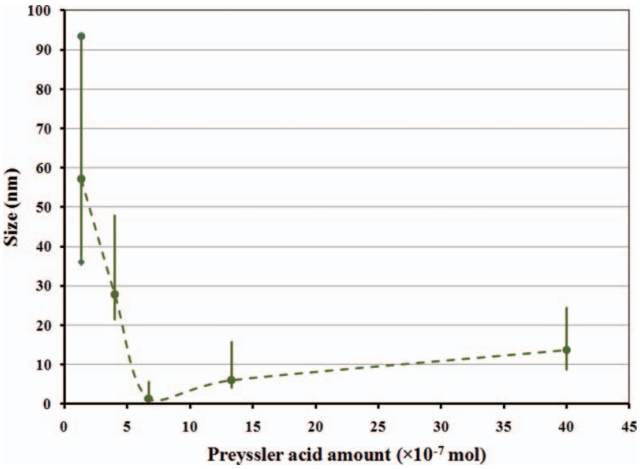

FIG. 4. Effect of Preyssler acid amount on the size of Au NPs ($[Au^{3+}] = 10^{-3}$ M) after 45-min irradiation (color figure available online).

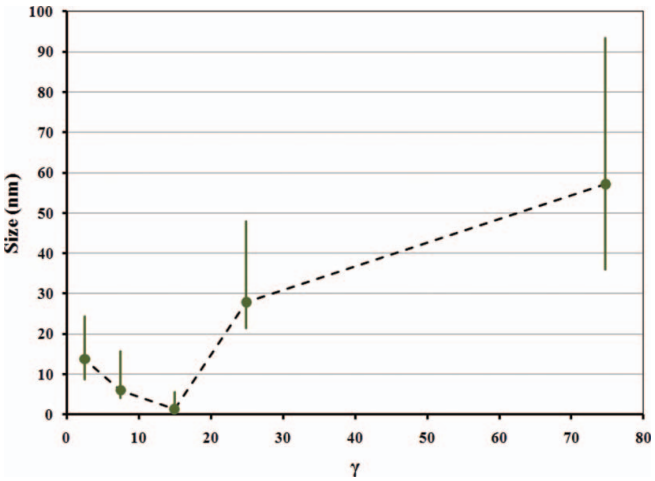

FIG. 5. Effect of $\gamma = [Au^{3+}]/[Preyssler]$ ratio on the size of Au NPs ($[Au^{3+}] = 10^{-3}$ M) after 45-min irradiation (color figure available online).

The fact in which smaller Au NPs are formed with increasing the initial amount of Preyssler implies that the nucleation process is enhanced more than the growth of these nanoparticles. In this range, our findings verify the results of other studies such as Troupis et al.[7,8,16] and Yang et al.[28] 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 formation of smaller nanoparticles. However, our results show that this is not valid in all the initial concentration range of Preyssler. As seen in Figure 4, increasing the Preyssler concentration above 6.6×10^{-7} M, the size of synthesized NPs exhibited a contrary trend. This finding verifies the results of our previous investigation[22] and also the study of Sun et al.[9] The reason for the opposing trend of large Au NPs may be due to higher coverage of Preyssler polyanions on the exterior surface of Au NPs at higher amount of Preyssler that reduce the reaction rate in Eq. 2.

In another word, the concentration of 6.6×10^{-6} M acts as a critical Preyssler acid amount in the synthesis of Au NPs under our experimental conditions. This value depends on the types of metal ions, POM, and other operating conditions such as temperature, pH, and ionic strength.

The previous finding can also be explained by the variation of $[Au^{3+}]/[Preyssler] = \gamma$ molar ratio. Figure 5 shows the dependency of nanoparticles diameter on the ratios of γ. As demonstrated in this figure, when γ <14.9, increasing the Preyssler 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 nanosystems, because the nucleation and growth sequences are both affected by the relative concentrations of the reducing agent and the precursor.[16] In our case, when γ <14.9, it seems by increasing the γ 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 14.9, producing larger nanoparticles.

Effect of Propan-2-ol Amount

Propan-2-ol serves as sacrificial reagent for the photoformation of 1-equivalent reduced Preyssler acid, POM(e), which further reacts with Au(III) to produce Au NPs. A control experiment was performed in which only 2 mL propan-2-ol was added to 10 mL dearated aqueous solution of $HAuCl_4$ and irradiated for 6 h. 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 UV-irradiated propan-2-ol is not responsible for the reduction of Au^{3+}.

Also, we have observed that in the presence of Preyssler acid when the amount of propan-2-ol was less than 1 mL, there was not any color change and no Au NPs were obtained. Therefore, the amount of propan-2-ol can affects the reaction rate and subsequently the size of the synthesized Au NPs. Figure 6 shows that at constant initial Au^{3+} ion concentration (10^{-3} M) and

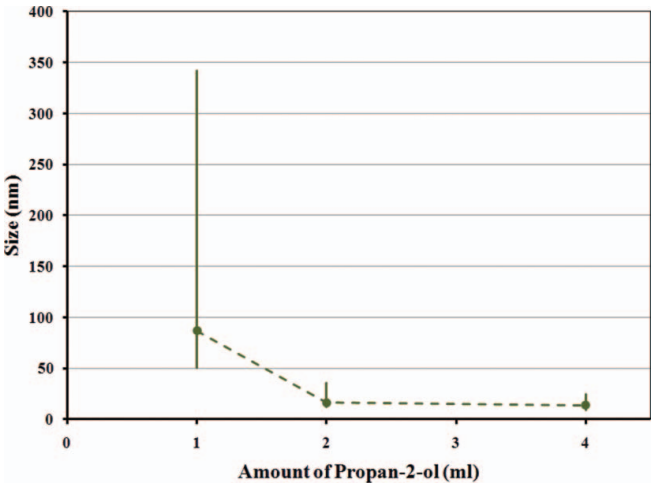

FIG. 6. Effect of propan-2-ol amount on the size of Au NPs ($[Au^{3+}] = 10^{-3}$ M, Preyssler $= 4 \times 10^{-6}$ mol) (color figure available online).

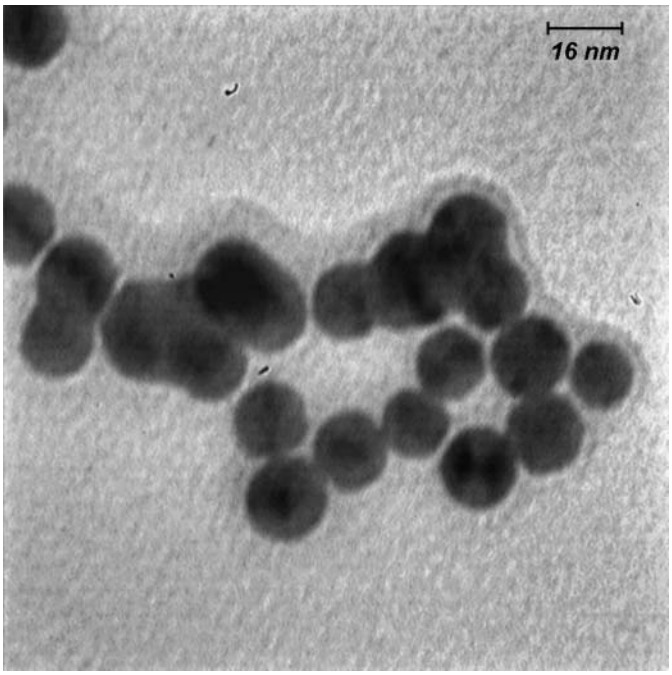

FIG. 7. TEM images of Au NPs after 45-min irradiation ($[Au^{3+}] = 10^{-3}$ M, Preyssler $= 6.7 \times 10^{-7}$ mol).

Preyssler quantity (4×10^{-6} mol), by increasing the propan-2-ol from 1 to 4 mL, smaller and more uniform nanoparticles were obtained. In fact, increasing the propan-2-ol amount helps nucleation to be faster. As seen in the figure, by utilizing 1 mL propan-2-ol, the obtained Au NPs are not uniform and their size varies between about 51 and 242 nm.

Characterization of Au NPs

For the experimental condition of $[Au^{3+}] = 10^{-3}$ M, Preyssler $= 6.7 \times 10^{-7}$ mol, and propan-2-ol $= 2$ mL, the obtained Au NPs were characterized by TEM and shown in Figure 7. The shapes of the gold nanoparticles are nearly uniform hexagonal. Also, the particle size distribution of these Au NPs is quantitatively displayed in a histogram shown in Figure 8. As seen, the particle size distribution indicates that the size of the Au NPs varied from about 13 to 43 nm, with a mean diameter of about 17 nm.

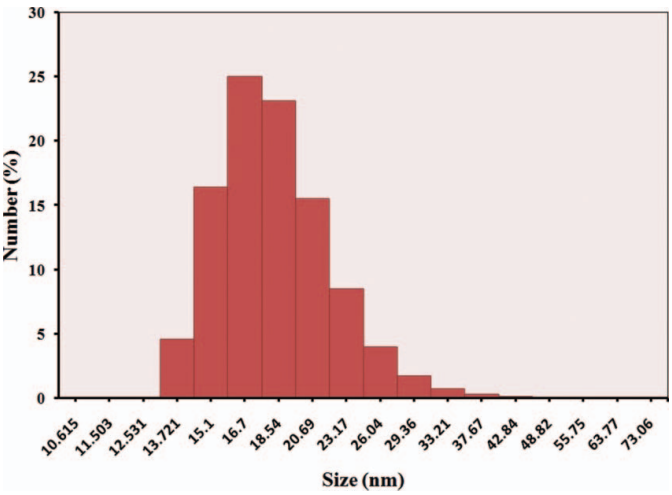

FIG. 8. Particle size distribution of Au NPs after 45-min irradiation (color figure available online).

CONCLUSIONS

Preyssler acid ($H_{14}[NaP_5W_{30}O_{110}]$) was used as an excellent green reducing agent and stabilizer in the synthesis of gold nanoparticles. Uniform and size-controlled gold nanoparticles were easily prepared by the simple photolysis of Preyssler/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 Preyssler, and prpan-2-ol amount. Faster reductions would result in smaller and more uniform hexagonal gold nanoparticles as exhibited by increasing the initial concentration of gold ions and the amount of propan-2-ol. It was also found that there is a critical ratio of $\gamma = [Au^{3+}]/[\text{Preyssler}]$, in which in its lower range, increasing the ratio leads to the formation of smaller nanoparticles and in its higher value, the contrary trend happened.

REFERENCES

1. Hutchings, G. J. Catalysis by gold. *Catal. Today* **2005**, *100*, 5–61.
2. Yu, C.; Chang, S.-S.; Lee, C.; Wang, C. R. Gold nanorods: electrochemical synthesis and optical properties. *J. Phys. Chem.* **1997**, *101*, 6661–6664.
3. Jana, N. R.; Gearheart, L.; Murphy, C. Evidence for seed-mediated nucleation in the chemical reduction of gold salts to gold nanoparticles. *J. Chem. Mater.* **2001**, *13*, 2313–2322.
4. Caruso, R. A.; Ashokkumar, M.; Grieser, F. Sonochemical formation of gold sols. *Langmuir* **2002**, *18*, 7831–7836.
5. Kim, F.; Song, J. H.; Yang, P. Photochemical synthesis of gold nanorods. *J. Am. Chem. Soc.* **2002**, *124*, 14316–14317.
6. Sharma, V. K.; Yngard, R. A.; Lin, Y. Silver nanoparticles: green synthesis and their antimicrobial activities. *Adv. Colloid Interface. Sci.* **2009**, *145*, 83–96.
7. Troupis, A.; Triantis, T.; Hiskia, A.; Papaconstantinou, E. Rate-redox-controlled size-selective synthesis of silver nanoparticles using polyoxometalates. *Eur. J. Inorg. Chem.* **2008**, 5579–5586.
8. Troupis, A.; Hiskia, A.; Papaconstantinou, E. Synthesis of metal nanoparticles by using polyoxometalates as photocatalysts and stabilizers. *Angew. Chem., Int. Ed.* **2002**, *41*, 1911–1913.
9. Sun, G.; Li, Q.; Xu, R.; Gu, J.; Ju, M.; Wang, E. Controllable fabrication of platinum nanospheres with a polyoxometalate-assisted process. *J. Solid State Chem.* **2010**, *183*, 2609–2916.
10. Bamoharram, F. F.; Ahmadpour, A.; Heravi, M. M.; Ayati, A.; Rashidi, H.; Tanhaei, B. Recent advances in application of polyoxometalates for the synthesis of nanoparticles. *Synth. Reac. Inorg. Met-Org. Nano-Met. Chem.* **2012**, *42*, 209–230.
11. Katsoulis, D. E. A survey of applications of polyoxometalates. *Chem. Rev.* **1998**, *98*, 359–387.
12. Papaconstantinou, E. Photochemistry of polyoxometallates of molybdenum and tungsten and/or vanadium. *Chem. Soc. Rev.* **1989**, *18*, 1–31.
13. Wang, E. B.; Hu, C. W.; Xu, L. *Introduction to Polyacid Chemistry*; Chemical Industry Press: Beijing, **1998**.
14. Weinstock, I. A. Homogeneous-phase electron-transfer reactions of polyoxometalates. *Chem. Rev.* **1998**, *98*, 113–170.

15. Hiskia, A.; Mylonas, A.; Papaconstantinou, E. Comparison of the photoredox properties of polyoxometallates and semiconducting particles. *Chem. Soc. Rev.* **2001**, *30*, 62–69.
16. Triantis, T.; Troupis, A.; Gkika, E.; Alexakos, G.; Boukos, N.; Papaconstantinou, E.; Hiskia, A. Photocatalytic synthesis of Se nanoparticles using polyoxometalates. *Catal. Today* **2009**, *144*, 2–6.
17. Bamoharram, F. F. Role of polyoxometalates as green compounds in recent developments of nanoscience. *Synth. Reac. Inorg. Met-Org. Nano-Met. Chem.* **2010**, *41*, 893–922.
18. Mandal, S.; Das, A.; Srivastava, R.; Sastry, M. Keggin ion mediated synthesis of hydrophobized Pd nanoparticles for multifunctional catalysis. *Langmuir* **2005**, *21*, 2408–2413.
19. Mandal, S.; Selvakannan, P. R.; Pasricha, R.; Sastry, M. Keggin ions as UV-switchable reducing agents in the synthesis of Au core-Ag shell nanoparticles. *J. Am. Chem. Soc.* **2003**, *125*, 8440–8441.
20. Niu, C.; Wu, Y.; Wang, Z.; Li, Z.; Li, R. Synthesis and shapes of gold nanoparticles by using transition metal monosubstituted heteropolyanions as photocatalysts and stabilizers. *Front. Chem. China*, **2009**, *4*, 44–47.
21. Sanyal, A.; Mandal, S.; Sastry, M. Synthesis and assembly of gold nanoparticles in quasi-linear lysine-keggin-ion colloidal particles. *Adv. Funct. Mater.* **2005**, *15*, 273–280.
22. Ayati, A.; Ahmadpour, A.; Bamoharram, F. F.; Heravi, M. M.; Rashidi, H. Photocatalytic synthesis of gold nanoparticles using preyssler acid and their photocatalytic activity. *Chin. J. Catal.* **2011**, *32*, 978–982.
23. Bamoharram, F. F.; Heravi, M. M.; and Meraji, M. Synthesis of silver nanoparticles in the presence of a green heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$, and their catalytic activity for photodegradation of methylene blue and methyl orange. *Int. J. Green Nanotechnol.: Phys. Chem.* **2009**, *1*, 26–31.
24. Ayati, A.; Ahmadpour, A.; Bamoharram, F. F.; Heravi, M. M.; Rashidi, H.; Tanhaei, B. Application of molybdophosphoric acid in size-controlled synthesis of gold nanoparticles under UV irradiation. *Int. J. Nanosci. Nanotechnol.* **2012**, *7*, 87–93.
25. Ayati, A.; Ahmadpour, A.; Bamoharram, F. F.; Heravi, M. M.; Rashidi, H.; Tanhaei, B. Application of a new photocatalyst in the preparation of silver nanoparticles and investigating their photocatalytic activity. *J. Nanostruct. Chem.* **2011**, *2*, 15–22.
26. Ayati, A.; Ahmadpour, A.; Bamoharram, F. F.; Heravi, M. M.; Rashidi, H. Optimization of the experimental conditions in synthesis of Au Nps using Preyssler heteropolyacid based on the Taguchi robust design. *NANO* **2012**, *7*, 1–10.
27. Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Jahangir, M.; Gharib, A. Preyssler catalyst,, $[NaP_5W_{30}O_{110}]^{14-}$: A green, efficient and reusable catalyst for esterification of salicylic acid with aliphatic and benzylic alcohols. *Appl. Catal. A: Gen.* **2006**, *302*, 42–47.
28. Yang, L.; Shen, Y.; Xie, A.; Liang, J.; Li, S.; Zhang, Q. Size- and shape-controlled synthesis and assembly of a silver nanocomplex in UV-irradiated TSA solution. *Eur. J. Inorg. Chem.* **2006**, 4658–4664.