

RESEARCH PAPER

A Green Approach to the Facile Synthesis of Colloidal Platinum Nanoparticles by Preyssler Polyoxometalate

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ABSTRACT

In the present study, platinum nanoparticles were synthesized through an effective, facile and green method using $H_{14}[NaP_5W_{30}O_{110}]$, a Preyssler-structured polyoxometalate, under UV light irradiation. Preyssler plays the roles of photocatalyst, reducing agent and stabilizer in the synthesis of Pt nanoparticles. The effect of different parameters, i.e. time, propan-2-ol volume, pH, molar ratio of Preyssler to Pt ions ($[Preyssler]/[Pt^{4+}]$) and temperature on the size of prepared nanoparticles were investigated. Under different conditions, platinum nanoparticles with minimum size of 13 nm were ultimately obtained. The nanoparticles were characterized by UV/Vis spectroscopy, particle size distribution, transmission electron microscopy and electron diffraction techniques. The results showed that the photocatalytic behavior of Preyssler was a propulsion factor in reducing the Pt^{4+} ions. The resultant NPs are covered with a Preyssler layer which contributes to the stabilization of NPs. It was shown that the subsequent increasing of NP size can be on account of partly increasing rate of NP growth compared to nucleation. Moreover, the stability of obtained nanoparticles was inspected.

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INTRODUCTION

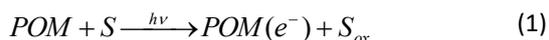
Metal nanoparticles are clusters of corresponding metal atoms with distinctive characteristic features. Amongst them, platinum nanoparticles (Pt NPs) have attracted great attention in the fields of energy production [1-3], environmental protection [4-6] and medicine [7-9], due to their exceptional catalytic and optical properties. These nanoparticles have been applied in fuel cells [3], petroleum industries [5], catalytic converters [6], biosensors [8] and drug delivery [9].

So far, various chemical approaches have been exploited for the synthesis of colloidal Pt NPs, such as photochemical [10, 11], sonochemical [12], polyol [13, 14] and reverse microemulsion [15] methods. Most of these methods suffered from some drawbacks, including high cost, high temperature, tedious work-up procedure, long reaction times and environmental problems [13, 14]. For example, the reaction mixture generally contained three reagents, platinum precursor, reductant and stabilizer. The most common reductants were alcohols, citrate, hydrazine

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and formaldehyde [7, 11, 13, 14, 16], that could not be restored and inevitably entered into the environment. Besides, the polymeric reagents were used as stabilizer [10, 11, 14, 16], which can decrease the catalytic activity of prepared Pt NPs. Accordingly, they rarely follow the green chemistry criteria that encouraged scientists to investigate different alternative for nanoparticles synthesis.

Polyoxometalates (POMs) are transient metal-oxygen clusters with various structures and exhibit considerable redox and photocatalytic properties [17-25]. POMs are large molecules with high anionic charge, which can tolerate several-electron exchanges without any alteration in their structures [17, 20, 21, 26, 27]. They are a green kind material that are harmless to the environment with respect to safety, corrosiveness, low waste and specially, separability. Under photo irradiation, these compounds can act as both an oxidizer for organic materials (S) and a reducer of metal ions (M^+) through Eqns. (1) and (2) respectively [20].



Consequently, many researchers have applied POMs for facile and green synthesis of highly surface-charged metal NPs, in which the POMs performed the multifunctional duties of photocatalyst, reducing and stabilizing agents [20, 22, 23, 25, 28-31]. POMs have different types, such as Keggin, Dawson, mixed valance, Preyssler, etc. with different chemical properties. Along with the various studies on the role of POMs in the synthesis of metal nanoparticles, Keggin and mixed-valance types of POMs have been exploited for the synthesis of Pt NPs. For instance, Troupis et al. have reported synthesis of Pt NPs at room temperature using $H_3[SiW_{12}O_{40}]$, a Keggin type of POMs [20]. In this regard, the role of Preyssler acid has been largely overlooked. This type of POM have remarkable properties, including strong Brønsted acidity with 14 acidic protons, high oxidation potential, high hydrolytic and thermal stability, non-corrosiveness, safety and substantial recyclability [25, 32]. In this assessment, we present our efforts for synthesizing Pt NPs with the assistance of Preyssler acid, $H_{14}[(NaP_5W_{30}O_{110})]$, using an one-pot reaction system in which Preyssler acts as photocatalyst, reductant and stabilizer with no need of surfactant.

MATERIALS AND METHODS

Synthesis of NPs

H_2PtCl_6 and propan-2-ol were obtained from Merck Company and used as received. Preyssler acid was synthesized according to the method described in previous work [33]. In a typical experiment, 50 mL of H_2PtCl_6 solution (2×10^{-4} M), Preyssler and 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. Temperature was regulated using water circulation around the cell. Ultimately, a colloid with a slight yellow color was appeared, indicating the formation of Pt NPs [34]. Similarly, several reactions were performed under different conditions to investigate the effect of different parameters, i.e. time, propan-2-ol volume, pH, molar ratio of Preyssler to Pt ions ($[Preyssler]/[Pt^{4+}]$) and temperature.

Characterization

UV/Vis spectra of NPs were obtained using Avantes Avaspec-3648 single beam instrument. The size of NPs was determined by a particle size analyzer VASCO instrument (Cordouan technology). Nanoparticles were inspected using Transmission Electron Microscopy (TEM) via Philips CM-120 apparatus.

RESULTS AND DISCUSSION

Under UV irradiation, Preyssler acid was activated and simultaneously undertook the reduction of Pt ions and formation of stable NPs. In this process a charge transfer from propan-2-ol to Pt^{4+} ions occurs via Preyssler acid that features a considerable photocatalytic activity. Herein, propan-2-ol plays acts as a sacrificial agent. For concise investigations, the UV/Vis absorption spectrum of the reactants mixture is measured before starting of the reaction and representatively shown in Fig. 1. In this figure, there is only one peak near 260 nm wavelength ascribed to the characteristic absorption band of $PtCl_6^{2-}$ [35-37].

Depicted in Fig. 2, the spectra of the reaction mixture at different stages of irradiation consist of two peaks in the range of 211-217 nm and 260-278 nm. Appearance of the former is due to the surface plasmon resonance of Pt NPs [13, 34, 38]. The latter can be caused by acetone produced from alcohol oxidation and also by the residue of $PtCl_6^{2-}$ [13]. Up to 2 h of irradiation, the resonance

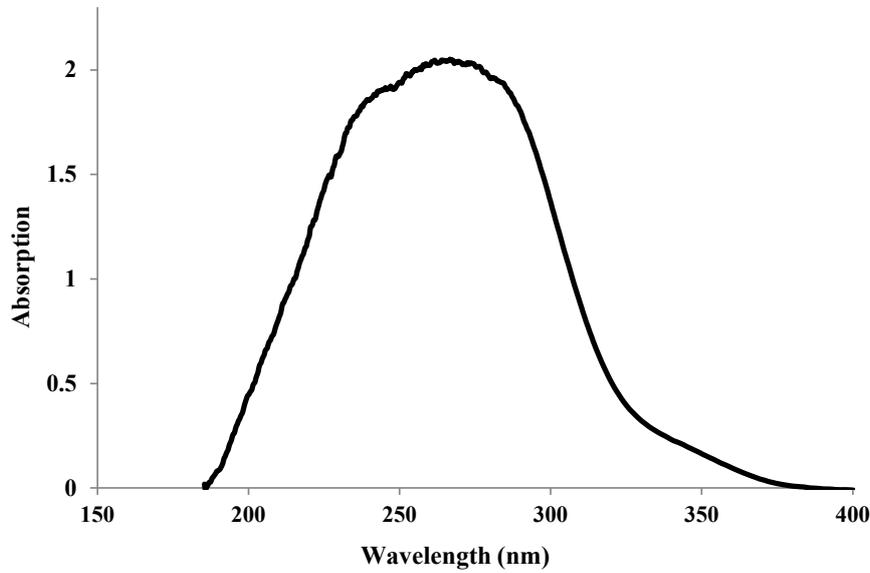


Fig. 1. UV-Vis absorption spectrum of the reactant.

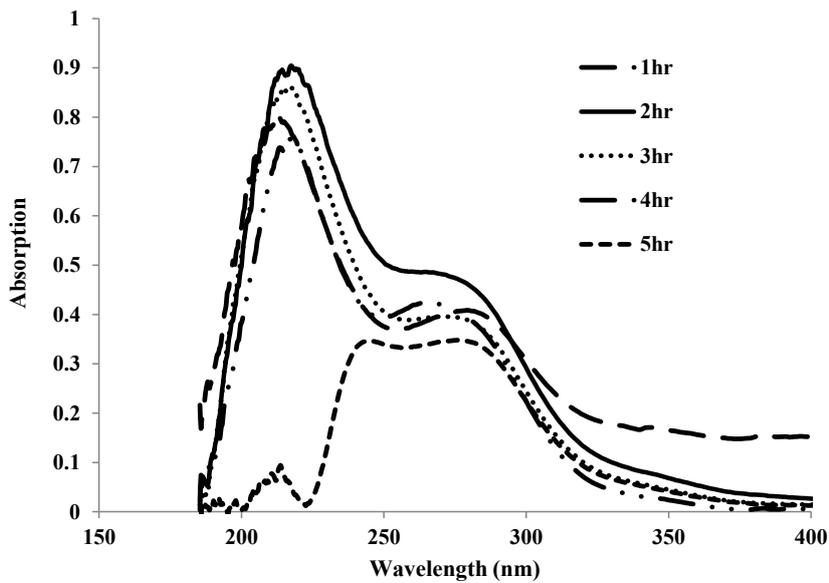


Fig. 2. UV-Vis spectra of the reaction mixture at different stages of irradiation ([Preyssler]/[Pt⁴⁺]: 0.1, propan-2-ol: 2 mL, pH: 2, temperature: 20°C).

intensity increased and then depleted. It can be due to the highest number of NPs which was achieved after 2 h [39]. More irradiation time led to aggregation of NPs, evidenced by a red shift and broadening particle size analyzing of the absorption peak of NPs after 5 h [13, 34]. This results were confirmed by particle size analyzing. After 2 and 5 h, the NPs with size of 20 and 93 nm were obtained respectively. In order to clarify the importance of the presence of Preyssler, a

control experiment was performed between 2 mL propan-2-ol and H₂PtCl₆ (2×10⁻⁴ M) in the absence of Preyssler acid. After 2 h irradiation, no change were observed in the absorption peak of the reactants.

The UV-vis spectra of synthesized Pt NPs using different amounts of propan-2-ol are shown in Fig. 3. In these experiments, four different volumes of propan-2-ol were examined, while the other parameters were kept constant. The maximal

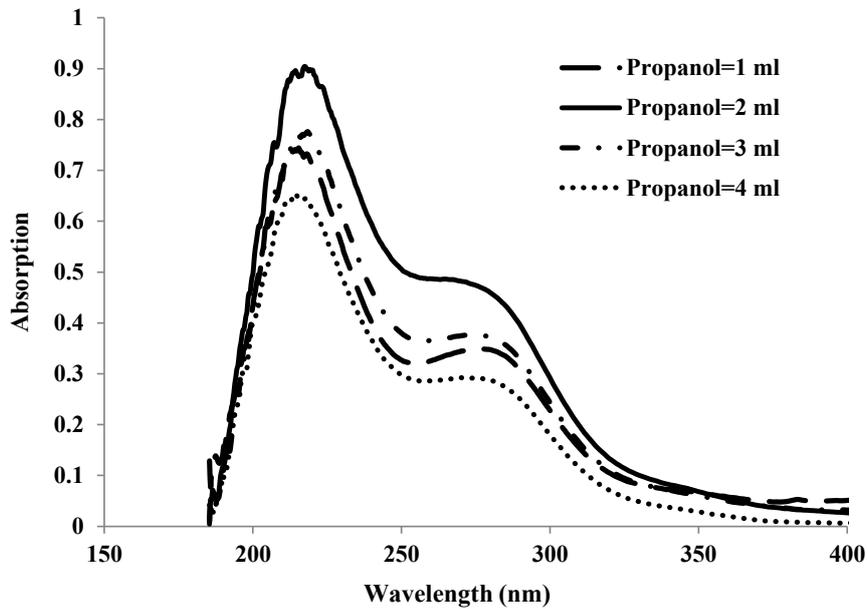


Fig. 3. The spectra of Pt NPs synthesized by using different volume of propan-2-ol ([Preyssler]/[Pt⁴⁺]: 0.1, time: 2 hr, pH: 2, temperature: 20°C).

resonance intensity was obtained by using 2 mL propan-2-ol, implying that the most populated colloid of NPs was formed. Indeed, altering the amount of propan-2-ol affects the nucleation rate [30]. Thus, the fraction of Pt atoms participates in nucleation, number of nuclei and consequently

number of NPs in colloid changes. By employing 2 and 4 mL of propan-2-ol, nanoparticles with a size of 20 and 25 nm was formed respectively.

By the same experiments, the effect of pH was also investigated (Fig. 4). It was found that increasing pH caused to reduction of resonance

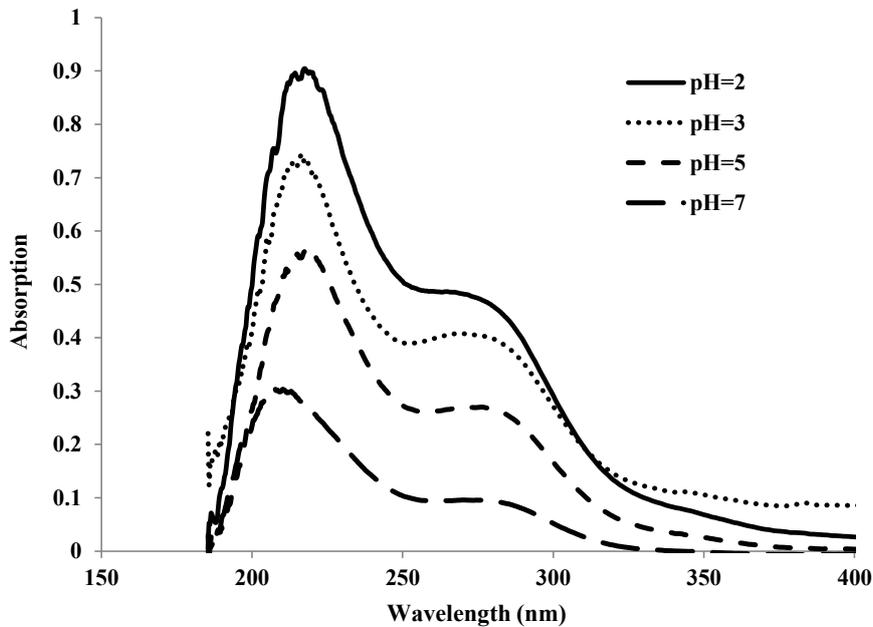


Fig. 4. UV-Vis spectra of Pt NPs synthesized at different pH ([Preyssler]/[Pt⁴⁺]: 0.1, time: 2 hr, propan-2-ol: 2 mL, temperature: 20°C).

intensity. Moreover, full-width at half-maximum (FWHM) of spectra at pH=7 was larger, as compared with lower amounts of pH. It was agree with the result of particle size analysis. At pH=2, a large number of NPs with average size of 20 nm were obtained, while at pH=7 a few NPs with size of 51 nm were produced. It is worth to note that lower pH values were found to be more effective in the synthesis of NPs. At low pH, the reduction of POMs can be catalytically enhanced by protons [40], followed by faster reduction of Pt ions. So, a large number of NPs with small size were produced.

The dependency of NP size to [Preyssler]/[Pt⁴⁺] and temperature was also examined. As displayed

in Fig. 5, when [Preyssler]/[Pt⁴⁺] increased, the size of obtained NPs firstly decreased to 16 nm (at [Preyssler]/[Pt⁴⁺] = 0.001) and then, slightly increased. Indeed, increasing the [Preyssler]/[Pt⁴⁺] ratio introduces more POMs to the reaction media which can increase the rate of reaction in Eqn. (2). The faster reaction would resulted to the smaller NPs [30]. In addition, POMs can prevent growth of NPs, as stabilizer. Much more increasing of [Preyssler]/[Pt⁴⁺] (>0.001) led to higher coverage of POMs on the exterior surface of NPs and resulted to decreasing the rate of equation (2) [30].

Therefore, rising of [Preyssler]/[Pt⁴⁺] ratio up to 1 resulted in the formation of very fine NPs trapped in a matrix of Preyssler (as shown in Fig.

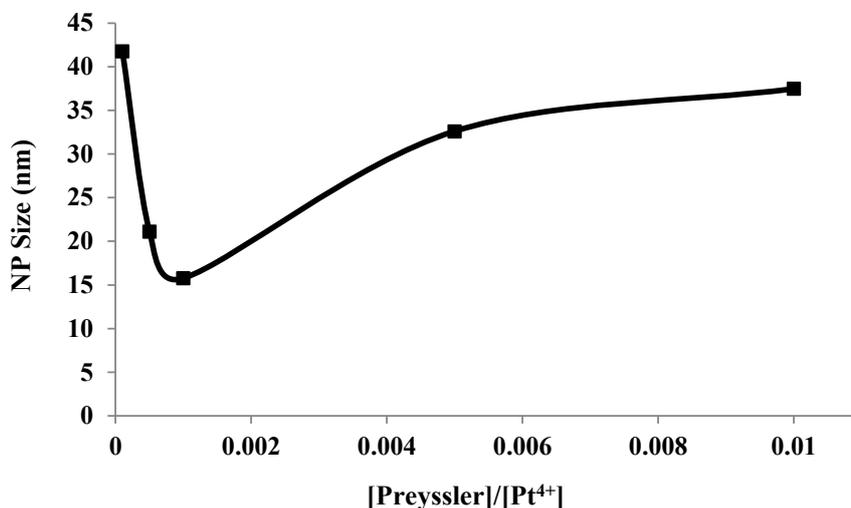


Fig. 5. Size of NPs versus [Preyssler]/[Pt⁴⁺] (time: 2 hr, propan-2-ol: 2 mL, pH: 2, temperature: 20°C).

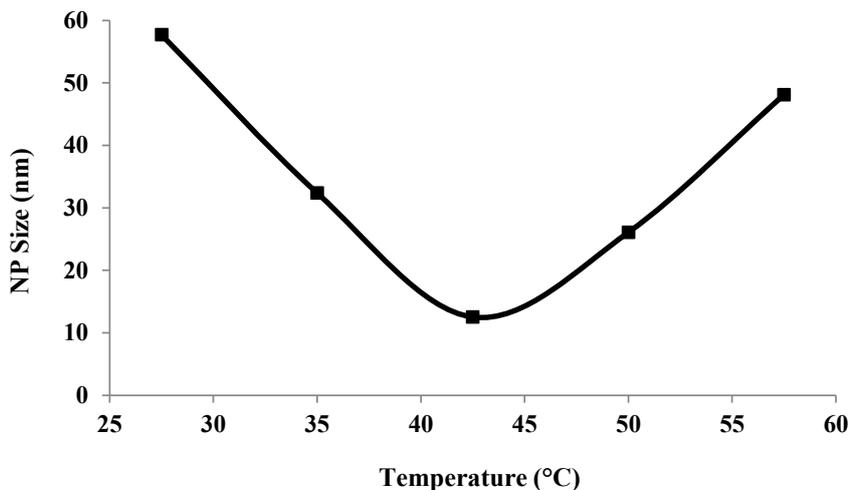


Fig. 6. Size of NPs versus temperature ([Preyssler]/[Pt⁴⁺]: 0.001, time: 2 hr, propan-2-ol: 2 mL, pH: 2).

6). The nanoparticles in this situation did not have any fortune of growth.

Fig. 7 displays the variation of the size of obtained nanoparticles with temperature. As can be see, with temperature increasing, the size of nanoparticles followed the same trend as shown in Fig. 5. Reduction of nanoparticles size is due to the growing kinetic energy of POMs and Pt ions with temperature which

improved the rate of equation (2) [39]. Subsequent increasing of NP size might be attributed to the partly increasing rate of nanoparticles growth compared to nucleation. Fig. 7 indicates that the minimum size of NPs is 13 nm, which was acquired at 42.5 °C. Particle size distribution of these nanoparticles is illustrated in Fig. 8. The inset in Fig. 8 shows the colloidal nanoparticles with a slight yellow color.

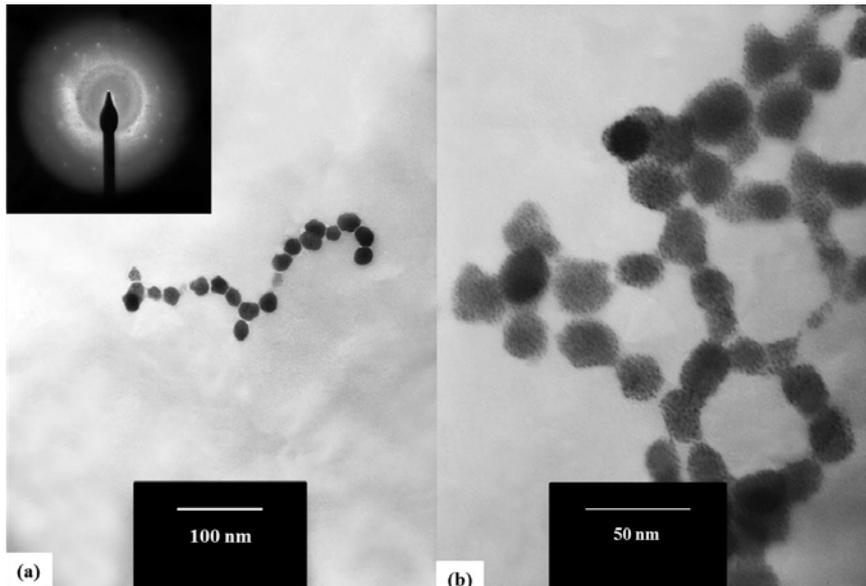


Fig. 7. (a) TEM image of Pt NPs, (b) TEM with high magnification. The inset: ED pattern of NPs.

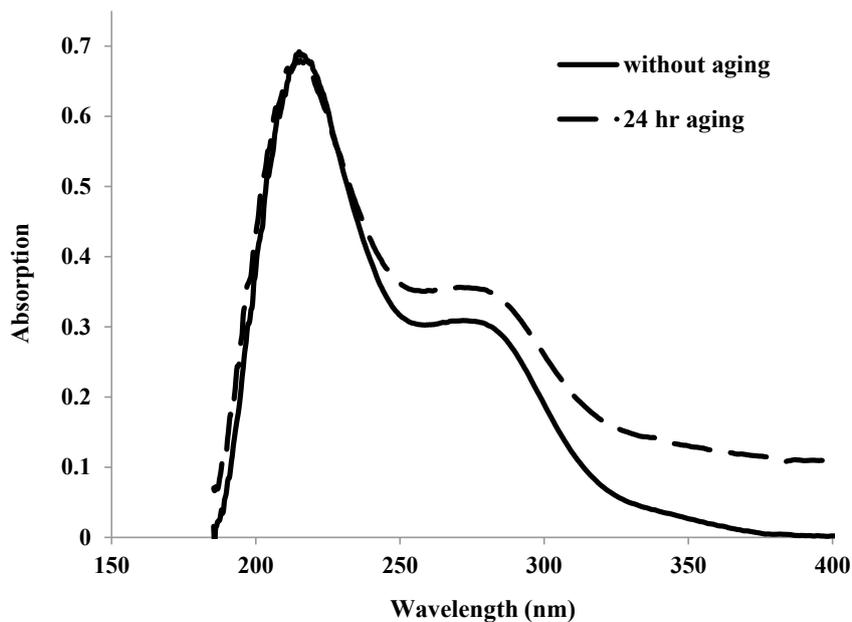


Fig. 8. UV-Vis spectra of NPs as soon as prepared (without aging) and after 24 hr aging.

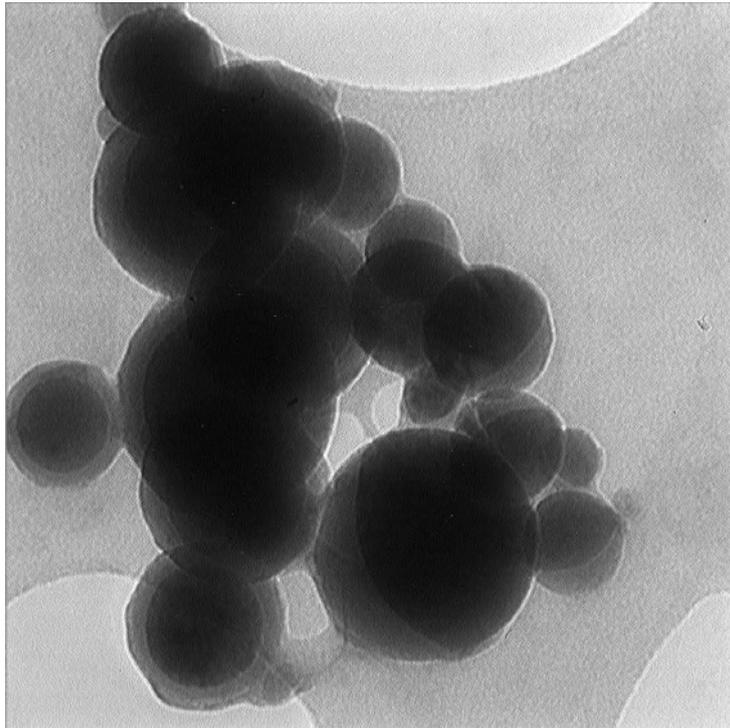


Fig. 9. TEM image of NPs covered with a POM layer.

Furthermore, TEM image of these NPs is shown in Fig. 9. It confirmed that the nanoparticles were formed with a uniform size. Also, the crystalline structure of Pt NPs was evidenced by ED pattern (the inset of Fig. 9).

In order to inspecting the stability of NPs, a control experiment was performed at a specific condition. Then absorption spectra of the prepared NPs was measured just at the end of the reaction (without aging) and also after 24 h aging. The results (see Fig. 10) indicated that no aggregation was discerned in the colloid. Furthermore, the TEM image of obtained Pt NPs (show in Fig. 11) clearly indicated that the nanoparticles were covered with a POM layer, which can stabilize the nanoparticles with their high negative charges.

CONCLUSIONS

Applying Preyssler acid as a green agent in the synthesis of Pt NPs, results in formation of highly stable NPs with uniform size. Preyssler acts as photocatalyst, reductant and stabilizer by oneself with no need to another contributing agent. The photocatalytic behavior of Preyssler was a propulsion factor in reducing the Pt^{4+} ions. The resultant NPs are covered with a Preyssler layer which contributes to the stabilization of NPs.

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CONFLICTS OF INTEREST

The Authors declares that there is no conflict of interest.

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