Asian Journal of Chemistry; Vol. 26, No. 23 (2014), 8079-8083

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17143

Preparation of Nanoclusters Encapsulating Ultrafine Platinum Nanoparticles

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Received: 30 January 2014; *Accepted*: 7 May 2014; *Published online*: 15 November 2014; AJC-16297

Platinum colloidal solutions have showed potential applications in various fields such as environment, biomedicine, catalysis, electronics, *etc*. According to a charateristic of poly(vinyl pyrolidone) (PVP) solution in which poly(vinyl pyrrolidone) chains are crosslinked and insoluble at higher temperatures with alkaline medium, we introduce a novel method to prepare nanoclusters like poly(vinyl pyrolidone)-based nanogels containing ultrafine platinum nanoparticles when hexachloroplatinic acid was reduced with mixture of poly(vinyl pyrolidone) and trisodium citrate at higher temperatures in alkaline medium. Formations of platinum nanoparticles and the nanoclusters were investigated under different pH and molecular weight of poly(vinyl pyrolidone). The colloidal solutions were characterized by UV-visible, XRD and TEM. Our results indicated that ultrafine platinum nanoparticles arround 2 nm encapsulated in nanoclusters when the preparation was conducted in alkaline media and platinum nanoparticles were produced at smaller size when lower molecular weight of poly(vinyl pyrrolidone) was used.

Keywords: Platinum nanoparticles, Green synthesis, Size control.

INTRODUCTION

Several kinds of metallic nanoparticles have recently been studied and used for many biomedical and industrial applications due to their novel and different properties such as optical, catalytic, magnetic, antimicrobial, *etc* compared to their bulk metallic form[1-3]. Among them, platinum nanoparticles exhibiting excellent electro/chemical catalytic properties and high stability that have been attracted much attention in practical applications such as catalyst for chemically synthetic processes and fuel cells[4,5]. A number of techniques have been reported for preparation of colloidal platinum nanoparticles such as chemical reduction method, sol-gel method, hydrothermal and solvothermal techniques, electrodeposition and electroless deposition[6-11]. It is well-known that platinum nanoparticles and other metallic nanoparticles offer specially chemical, physical and biological properties as prepared at small sizes due to the increase in surface area of the nanoparticles. Therefore several approaches for preparation of the platinum nanoparticles have been developed to obtain ultrafine size which could be used to improve yield of the catalytic and electrocatalytic reactions or target this purpose[5,12-14]. One of these approaches is preparation of platinum nano-particles-encapsulated nanoclusters. Fan *et al.*[15] prepared nanocluster containing small platinum nanoparticles in poly(vinyl pyrrolidone) solution of water and ethanol through the photodecomposition of H_2PtCl_6 by irradiation of femtosecond laser. In their study, they just studied the intense irradiation of femtosecond laser effected on morphology of the formed platinum nanoparticles. They didn't explain the reason of forming platinum nanoparticles encapsulated nanocluster. Nanocluters containg platinum nanoparticles were also produced from the coat protein of tobacco mosaic virus[16]. In general, when the platinum nanoparticles were encapsulated in nanoclusters being small size and narrow size distribution.

In recent years, subjecting to a green chemical engineering and environmental protection, several green synthetic methods for metallic nanoparticles have recently been emerging in which water is used as solvent and reducing agent is more environmentally-friendly or biosynthetic systems is exploited[17]. According to these methods, platinum nanoparticles colloidal solution could be prepared with use of environmentally-friendly reducing agents and biosystems[18,19]. However, preparation of platinum nanoparticles colloidal solution in water media still hasn't been reported yet.

In this work, platinum colloidal solutions at small size in diameter have been synthesized rapidly in water media with precursor of hexachloroplatinic acid (H_2PtCl_6), poly(vinyl pyrrolidone) capping polymer and trisodium citrate reducing agent. Morphology and controlled size of platinum nanopar-

ticles were investigated in varying different molecular weights of poly(vinyl pyrrolidone), amount of citrate and pH to offer a suitable condition to platinum nanoparticles and ultrafine platinum nanoparticles in nanoclusters.

EXPERIMENTAL

Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 99 %) was purchased from Prolabo (France). Poly(vinyl pyrrolidone) (PVP) (1,000,000 g/mol, 1000 k) was supplied by Aldrich (Belgium), poly(vinyl pyrrolidone) (55,000 g/mol, 55 k) was obtained from Merck (Germany) and poly(vinyl pyrrolidone) (40,000 g/mol, 40 k) was purchased from Loba Chemie (India). Trisodium citrate (99 %) was supplied by acros organics.

Synthesis of platinum nanoparticles: In the typical synthesis, 0.02 g of poly(vinyl pyrrolidone) (with differences of MW) was dissolved in 40 mL of H_2O milipore under stirring and then adjusted to pH 7. Hexachloroplatinic acid 4.8×10^{-4} M (250 µL) was added into poly(vinyl pyrrolidone) solution and stirred for 10 min. Then, the beaker containing the mixture was placed in the center of microwave oven (2450 MHz). When this solution reached the temperature around 80 °C, then microwave oven was turned off, an aqueous solution trisodium citrate 0.1 M (0.5, 1, 1.5 or 2 mL) was added into the mixed solution under magnetic stirring. The colour of solution immediately changed from yellow to dark brown. The colloidal platinum nanoparticles solution was obtained after 10 min and then characterized with UV-visible, XRD and TEM. Effect of pH and molecular weight of poly(vinyl pyrrolidone) on formation of platinum nanoparticles and ultrafine platinum nanoparticles in nanoclusters were evaluated using the same method.

Characterization of the nanoparticles: UV-visible absorption spectrum of the prepared solutions were measured by UV-visible spectroscopy (Zasco V670). TEM images were taken by JEM-1400, samples for TEM were prepared by dropping of Pt solution onto a carbon-coated Cu grid, followed by slow evaporation of solvent at ambient additions. Histogram of the particles size distribution and average diameter were obtained by measuring about 50 particles. XRD spectrum of the platinum nanoparticles were characterized by using D8 Advanced Bragg X Ray powder diffraction with CuK_α radiation.

RESULTS AND DISCUSSION

Effect of amount of trisodium citrate on preparation of platinum nanoparticles at pH 7: At pH 7, amount of trisodium citrate reductant indicated a significant influence on formation of platinum nanoparticles as shown in Fig. 1, in which increment in trisodium citrate resulted in increasing absorbance of the colloidal solution due to the increased amount of platinum nanoparticles formation[20,21]. This is explained that trisodium citrate is a reducing agent for platinum ions in the experimental condition. A highest amount of platinum nanoparticles formation could be observed when using 2 mL of trisodium citrate 0.1 M. However, there is seem to be no significant change in the peak position (224-226 nm) at different concentration of trisodium citrate. So this could indicate that concentration of reductant didn't affect the size of platinum nanoparticles. Fig. 1 also shows a single and strong absorption peak at 224-226 nm and an unsteady absorption peak around 280 nm due to electronic transitions from HOMO to LUMO species. These absorption peaks are more cleared when platinum nanoparticles were measured in organic solvents[20]. According to some previous studies, this is a characteristic of platinum nanoparticles that were were synthesized with (electro) chemical method[20,22].

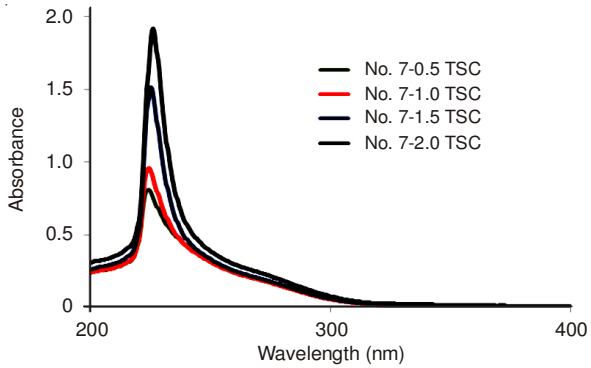

Fig. 1. UV-visible Absorption spectra of synthesized platinum nanoparticles with the different concentrations of trisodium citrate (0.5-2.0 mL of 0.1 M solution) at pH = 7

X-ray powder diffraction pattern of platinum nanoparticle was reduced by trisodium citrate (2 mL of 0.1 M solution) exhibiting diffraction at 2θ between 20-85° as shown in Fig. 2. The X-ray diffraction pattern confirmed the formation of face-centered-cubic (fcc) at 2θ of 40°; 46,5° and 68°, 81° representing (111), (200), (220) and (311) planes of fcc structure of platinum metal. All the peaks are well matched with the standard sample.

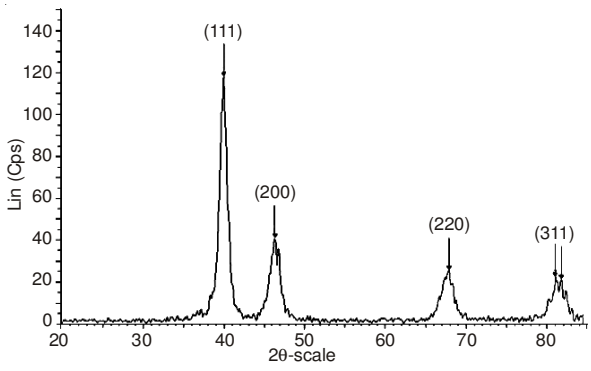

Fig. 2. X-ray diffraction (XRD) pattern of the platinum nanoparticles

Effect of the used poly(vinyl pyrrolidone) molecular weight and pH on size of platinum nanoparticles: Fig. 3 exhibited UV absorption of platinum nanoparticles colloidal solutions prepared in the presence of poly(vinyl pyrrolidone) protecting polymers. It indicates that a lower amount of platinum nanoparticles formation when capping poly(vinyl pyrrolidone) was used with higher molecular weight. This could be due to polymer with higher molecular weight tend to coil together, resulting in reducing its protective ability. Therefore, nanoparticles easily collided and agglomerated together to increase the particle size and reduce the number of nanoparticles. This explanation was clarified with TEM images of platinum nanoparticles in the colloidal solutions in which shows that the smallest size of the platinum nanoparticles could

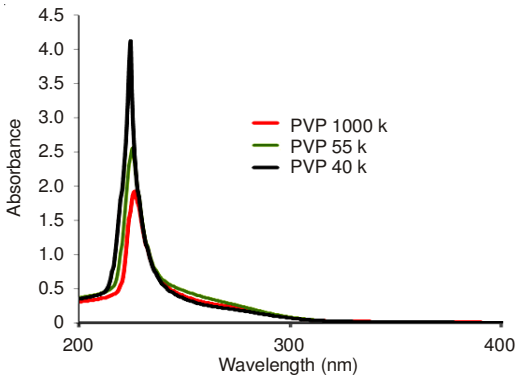

Fig. 3. UV-visible Absorption spectra of platinum nanoparticles colloidal solution in presence of poly(vinyl pyrrolidone) 40 k and trisodium citrate (2 mL of 0.1 M solution) at pH = 7

obtained when the experiment was conducted in the presence of a lowest molecular weight of poly(vinyl pyrrolidone) (Mw 40 k) (Fig. 4).

When the reduction was conducted at a higher pH (pH 9), Fig. 5 shows a single and strong absorption peak at 224-226 nm. This is also preferred with UV-visible absorption characteristic of platinum nanoparticles were synthesized with (electro) chemical method[20,22]. UV-visible absorption demonstrated that the peak intensity almost does not change at different molecular weight of used poly(vinyl pyrrolidone). Moreover, there is no significant change in absorption peak position. The molecular weight of poly(vinyl pyrrolidone)s didn't affect the number of platinum nanoparticles formation. However, TEM images of the platinum nanoparticles are shown in Fig. 6 indicating a slightly difference in size.

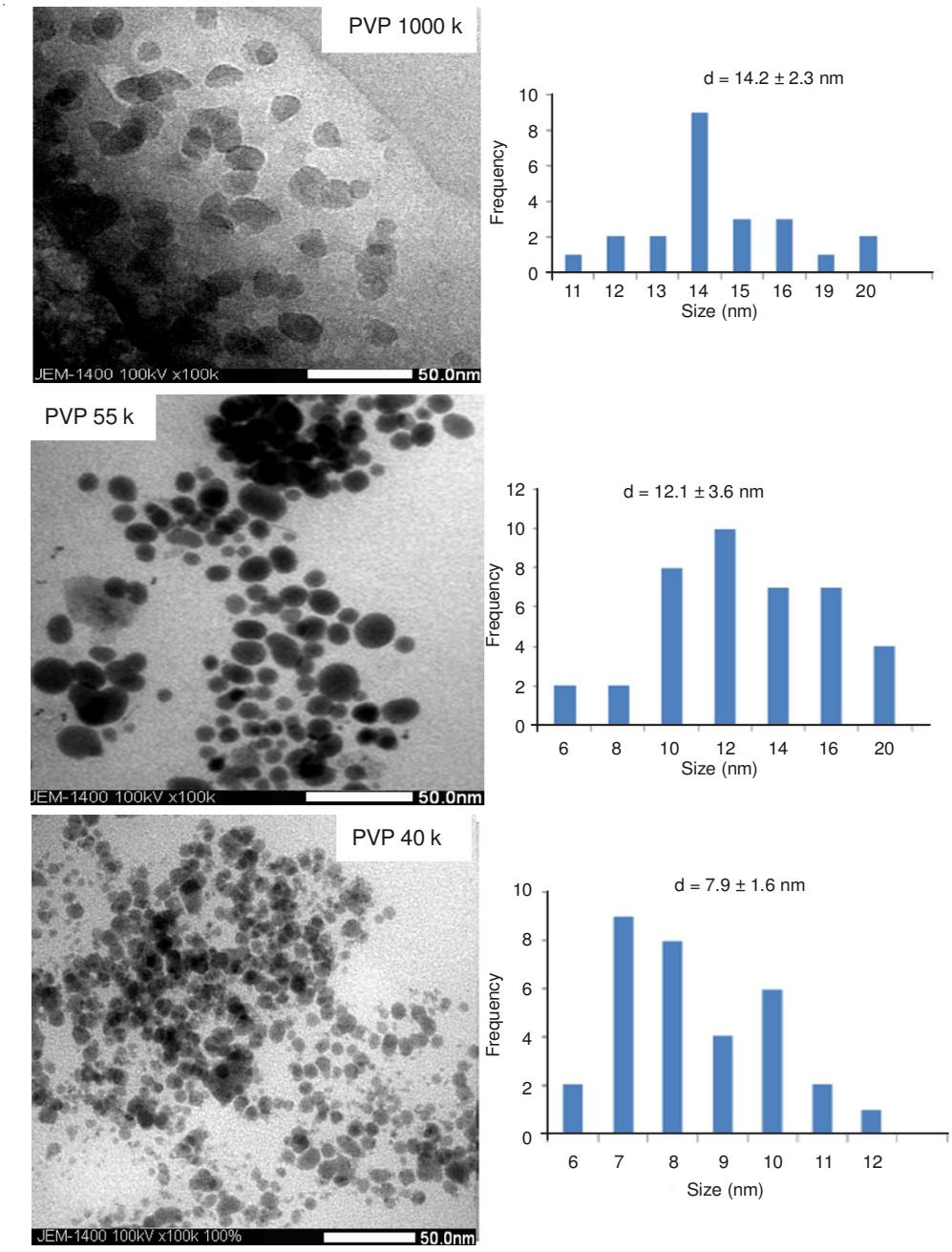

Fig. 4. TEM images and distribution histograms of platinum nanoparticles at pH = 7: in the presence of poly(vinyl pyrrolidone) 1000 k, PVP 55 k and PVP 40 k

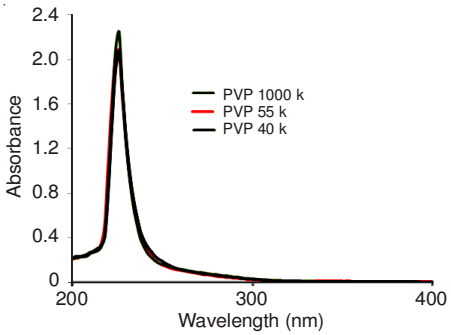

Fig. 5. UV-visible absorption spectra of synthesized platinum nanoparticles with the different poly(vinyl pyrrolidones) (1000 k, 55 and 40 k) at pH = 9

Platinum nanoparticles were produced at smaller size when lower molecular weight of poly(vinyl pyrrolidone) was used. In the experimental condition, the formed platinum nanoparticles have smaller size (2-4 nm) in comparison with in pH 7 environment (8-14 nm) and the particles were encapsulated in nanoclusters. These results could be explained that poly(vinyl pyrrolidone) polymers gradually become to be crosslinked and insoluble at higher temperatures with alkaline medium[23,24]. Trisodium citrate is under tribasic form (pH of solution-9) which have also been well-performed in its roles as a reductant and dispersant. Therefore, the ultrafine formed platinum nanoparticles were encapsulated poly(vinyl pyrrolidone)-based nanogel.

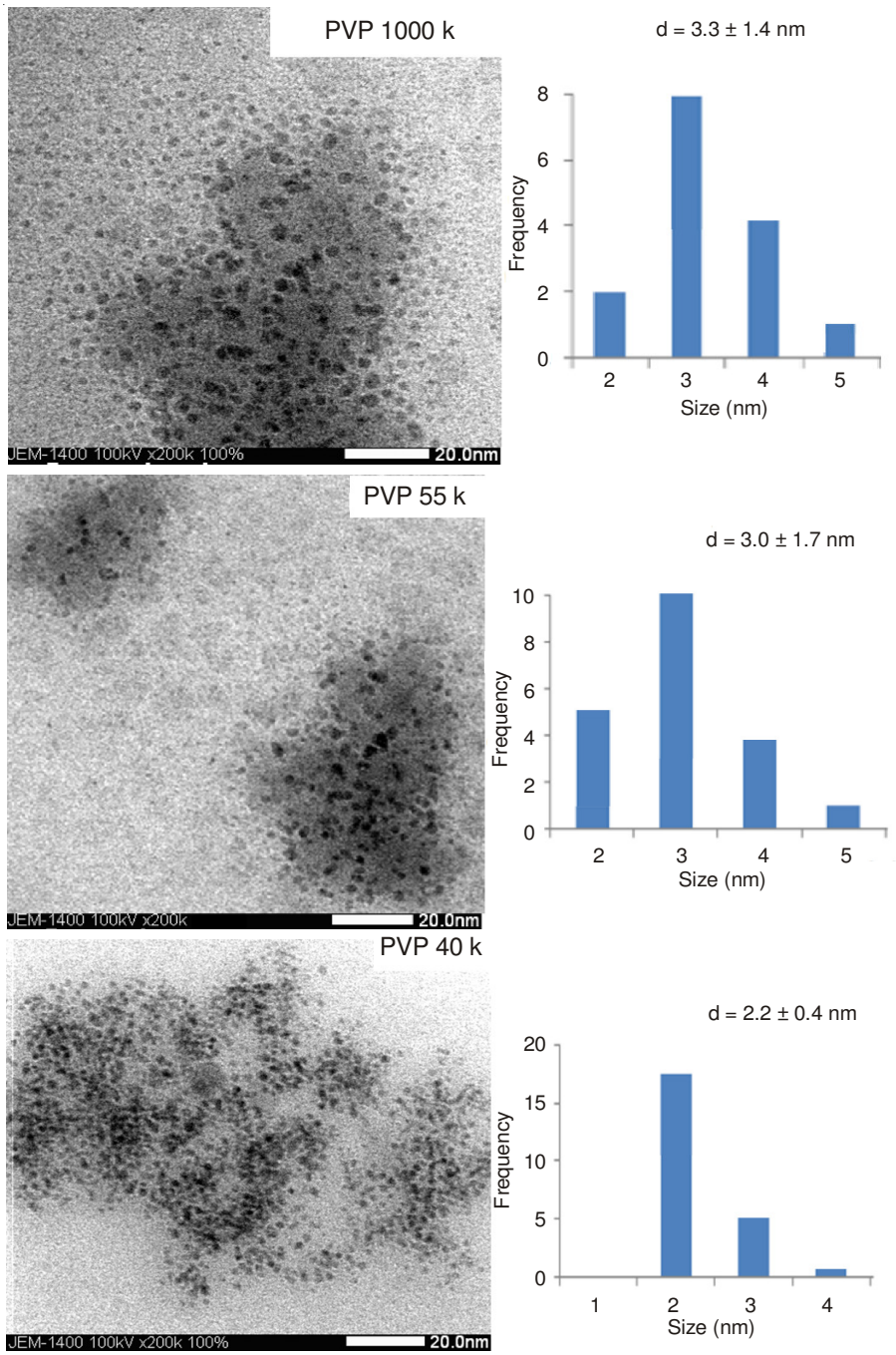

Fig. 6. TEM images and distribution histograms of platinum nanoparticles at pH = 9: in the presence of poly(vinyl pyrrolidone) 1000 k, PVP 55 k and poly(vinyl pyrrolidone) 40 k

This explanation also confirmed with experiments that were done at pH 11 (Fig. 7) at which UV-visible absorption is similar to pH 9. This concluded that nanoclusters encapsulating the small size of platinum nanoparticles (2-4 nm in diameter) could be prepared in the presence of poly(vinyl pyrrolidone) solutions at higher temperature and basic pH. Formation of nanoclusters encapsulating the ultra platinum nanoparticles will be significant in preparation of the metallic nanoparticle with well-controlled size for practical applications because the nanoparticle was entrapped in the nanogel particles and therefore its size couldn't increase in synthetic and storage progress.

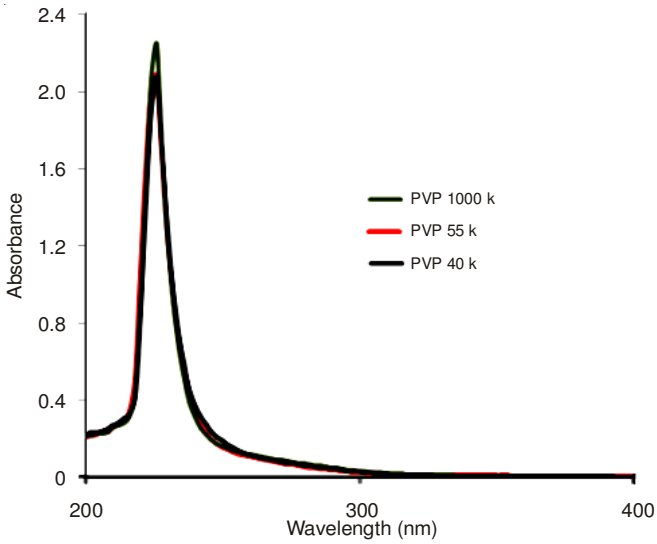

Fig. 7. UV-visible absorption spectra of synthesized platinum nanoparticles with the different poly(vinyl pyrrolidones) (1000 k, 55 and 40 k) at pH = 11

Conclusion

Platinum colloidal solutions have been rapidly synthesized in water media under microwave irradiation. The synthesized platinum colloidal solutions were characterized by XRD, UV-visible and TEM. The optimal experiment condition indicated that nanoclusters encapsulating the small size platinum nanoparticles (2 nm in diameter) could be prepared at basic media. The method will be significant in preparation of the metallic nanoparticle with well-controlled size and its storage for practical applications because of entrapment of the nanoparticle in the poly(vinyl pyrrolidone)-based nanogel.

ACKNOWLEDGEMENTS

This research is funded by Department of Science and Technology - Dongnai province No: 09/HĐ-SKHCN.

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