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A Novel One-Step Green Method to Synthesis of Palladium Nanoparticles †

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Abstract: Palladium nanoparticles (PdNPs) are one of the most attractive metal nanomaterials because of their excellent physicochemical properties. PdNPs have been studied for many different applications such as Suzuki cross-coupling reactions, hydrogen purification/storage/sensing, CO oxidation, fuel cells, prodrug activation, and antimicrobial therapy. Recently, PdNPs have been explored as photo-absorbers for photothermal therapy and photoacoustic imaging in the treatment of cancer disease. Herein, we reported a scalable, efficient, green, and one-step method to synthesis PdNPs. The chitosan polymer was used as a stabilizer and vitamin C was used as a reducing agent. Interestingly, the reaction temperature can be adjusted to the size of PdNPs. When the reaction temperature was increased from 25 °C to 95 °C, the morphology of resulted PdNPs changed from flower shape to spherical shape and their nanoparticles sizes decreased from 64 nm to 29 nm. The characterization revealed that the obtained PdNPs were relatively uniform in size, shape, and stable in aqueous solution.

Keywords: green methods; low-temperature method; palladium nanoparticles; various sizes; photothermal behavior; high photothermal conversion efficiency

1. Introduction

Palladium nanoparticles (PdNPs) are gaining attention due to their good physicochemical properties, such as high catalytic activity, good chemical stability, high thermal stability, and low cost [1,2]. They have been discovered in different including Suzuki cross-coupling reactions [3], hydrogen purification/storage/sensing [4], CO oxidation [5], and fuel cells [6], prodrug activation [7,8], antimicrobial therapy [7,9,10], photothermal therapy [7,11], and photoacoustic imaging [11,12].

The reported methods for preparation of PdNPs are complicated [13], toxic reductants [13–17], high-temperature conditions (e.g., 300 °C) [18,19], and long-time process [20]. The effective green method for synthesis PdNPs is needed.

Here, we reported a new method for the synthesis of spherical PdNPs. This method is scalable, green, low-temperature, and one-step. We utilized the chitosan (CS) as a stabilizer, vitamin C as a reducing agent, and water as a solvent. Interestingly, the reaction temperature was increased from 20 °C to 95 °C, the morphology of obtained PdNPs changed from flower shape to spherical shape and their size decreased from 64 nm to 29 nm. The resulted PdNPs were quite uniform in size, shape, and stable in aqueous solution.

2. Materials and Methods

2.1. Materials

Palladium chloride (PdCl2), chitosan (50 to 190 kDa, 75–85% degree of deacetylation), hydrochloric acid (HCl), and L-ascorbic acid (AA) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Synthesis of PdNPs

Firstly, the $HPdCl_4$ 0.01 M solution was prepared by adding 89 mg $PdCl_2$ to 50 mL DW containing 82 µL HCl 37%. After that, 2 mg CS and 50 mg AA were added to 15 mL DW to obtain an AA-CS solution. Then, AA-CS solution was preheated in the stirring mantle to the setup temperature (20 °C, 50 °C, 75 °C, and 95 °C). Next step, 10 mL $HPdCl_4$ 0.01 M was dropped into the preheated AA-CS solution. After 5 min of heating, the resulted solution was naturally cooled down to room temperature. PdNPs were collected by centrifugation and were washed with distilled water, and were dried in a vacuum to obtain the powder.

2.3. Characterization

The morphologies of PdNPs were obtained by Field-emission transmission electron microscopy (FETEM, JEOL JEM-2010 microscope, Japan). The size distribution of PdNPs was analyzed by an electrophoretic light scattering spectrophotometer (ELS-8000, OTSUKA Electronics Co. Ltd., Osaka, Japan). UV-Vis spectra of PdNPs solutions were recorded by a UV-Vis spectroscopy (Thermo Biomate 5 Spectrophotometer).

3. Results and Discussion

As shown in Figure 1, both AA-CS and HPdCl4 solutions have absorption peaks below 525 nm. There was a presence of a broadband absorption after 525 nm in all four temperature conditions.

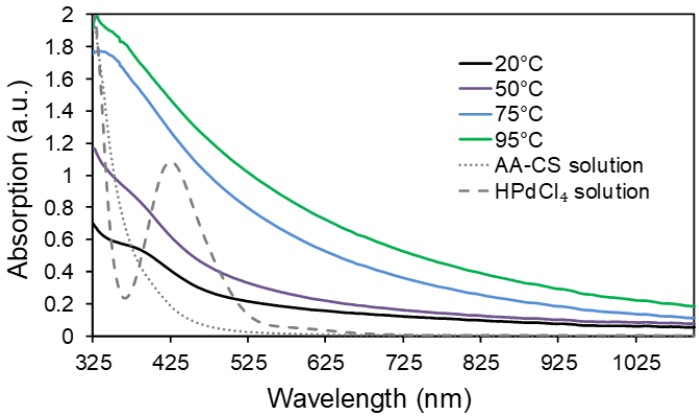

Figure 1. The UV-Vis absorption spectra of AA-CS solution, HPdCl4 solution, and PdNPs solutions from four different temperature synthesis conditions.

TEM images and size distribution of obtained PdNPs from four experimental conditions were shown in Figures 2 and 3, respectively. PdNPs had the flower shape at 20 °C experimental condition; but, the spherical shape was observed from experiments at 50 °C, 75 °C, and 95 °C. The hydrodynamic average sizes of PdNPs obtained from experiments at 20 °C, 50 °C, 75 °C, and 95 °C were 63.4 nm, 48.5 nm, 42.5 nm, and 29.6 nm, respectively.

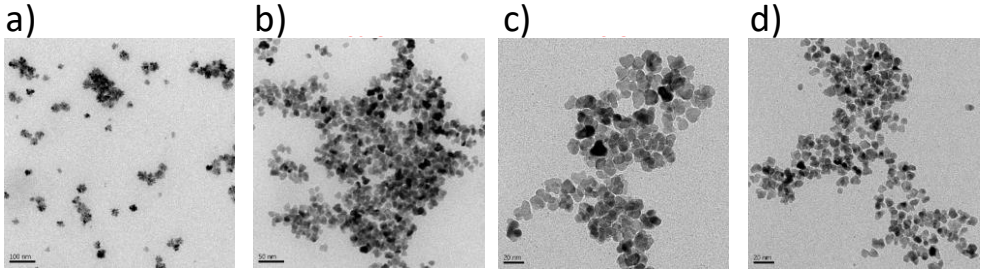

Figure 2. TEM images of PdNPs from four experiments: (**a**) 20 °C, (**b**) 50 °C, (**c**) 75 °C, and (**d**) 95 °C.

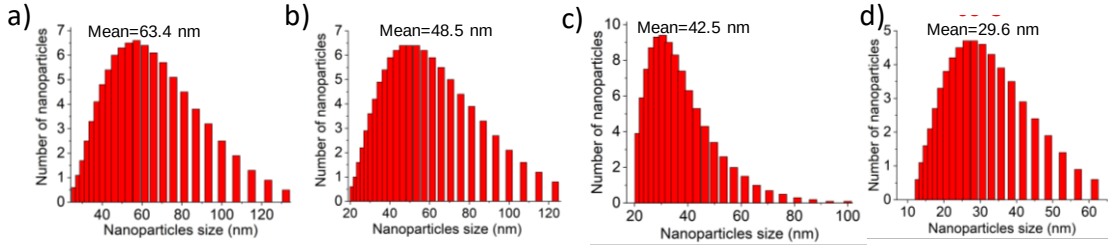

Figure 3. Size distribution of PdNPs from four experiments: (**a**) 20 °C, (**b**) 50 °C, (**c**) 75 °C, and (**d**) 95 °C.

4. Conclusions

In conclusion, we reported a simple, green, and low-temperature approach for the synthesis of the PdNPs. The reaction temperature plays an important role in controlling the size of PdNPs. The resulted PdNPs have a size from 64 nm to 29 nm.

References

1. Chen, A.; Ostrom, C. Palladium-Based Nanomaterials: Synthesis and Electrochemical Applications. *Chem. Rev.* **2015**, *115*, 11999–12044, doi:10.1021/acs.chemrev.5b00324.
2. Long, N.V.; Nguyen, C.; Hirata, H.; Ohtaki, M.; Hayakawa, T.; Nogami, M. Chemical synthesis and characterization of palladium nanoparticles. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2010**, *1*, doi:10.1088/2043-6262/1/3/035012.
3. Suzuki, A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. *J. Organomet. Chem.* **1999**, *576*, 147–168, doi:10.1016/S0022-328X(98)01055-9.
4. Adams, B.D.; Chen, A. The role of palladium in a hydrogen economy. *Mater. Today* **2011**, *14*, 282–289, doi:10.1016/S1369-7021(11)70143-2.
5. Kim, J.Y.; Jin, M.; Lee, K.J.; Cheon, J.Y.; Joo, S.H.; Kim, J.M.; Moon, H.R. In situ-generated metal oxide catalyst during CO oxidation reaction transformed from redox-active metal-organic framework-supported palladium nanoparticles. *Nanoscale Res. Lett.* **2012**, *7*, 461–461, doi:10.1186/1556-276X-7-461.
6. Long, N.V.; Thi, C.M.; Yong, Y.; Nogami, M.; Ohtaki, M. Platinum and palladium nano-structured catalysts for polymer electrolyte fuel cells and direct methanol fuel cells. *J. Nanosci. Nanotechnol.* **2013**, *13*, 4799–4824, doi:10.1166/jnn.2013.7570.
7. Dumas, A.; Couvreur, P. Palladium: A future key player in the nanomedical field? *Chem. Sci.* **2015**, *6*, 2153–2157, doi:10.1039/c5sc00070j.
8. Weiss, J.; Fraser, C.; Rubio-Ruiz, B.; Myers, S.; Crispin, R.; Dawson, J.; Brunton, V.; Patton, E.; Carragher, N.; Unciti-Broceta, A. N-Alkynyl Derivatives of 5-Fluorouracil: Susceptibility to Palladium-Mediated Dealkylation and Toxigenicity in Cancer Cell Culture. *Front. Chem.* **2014**, *2*, 56, doi:10.3389/fchem.2014.00056.
9. Adams, C.P.; Walker, K.A.; Obare, S.O.; Docherty, K.M. Size-dependent antimicrobial effects of novel palladium nanoparticles. *PLoS ONE* **2014**, *9*, e85981, doi:10.1371/journal.pone.0085981.

10. Manikandan, V.; Velmurugan, P.; Park, J.-H.; Lovanh, N.; Seo, S.-K.; Jayanthi, P.; Park, Y.-J.; Cho, M.; Oh, B.-T. Synthesis and antimicrobial activity of palladium nanoparticles from Prunus × yedoensis leaf extract. *Mater. Lett.* **2016**, *185*, 335–338, doi:10.1016/j.matlet.2016.08.120.
11. Phan, T.T.V.; Hoang, G.; Nguyen, V.T.; Nguyen, T.P.; Kim, H.H.; Mondal, S.; Manivasagan, P.; Moorthy, M.S.; Lee, K.D.; Junghwan, O. Chitosan as a stabilizer and size-control agent for synthesis of porous flower-shaped palladium nanoparticles and their applications on photo-based therapies. *Carbohydr. Polym.* **2019**, *205*, 340–352, doi:10.1016/j.carbpol.2018.10.062.
12. Bharathiraja, S.; Bui, N.Q.; Manivasagan, P.; Moorthy, M.S.; Mondal, S.; Seo, H.; Phuoc, N.T.; Vy Phan, T.T.; Kim, H.; Lee, K.D.; et al. Multimodal tumor-homing chitosan oligosaccharide-coated biocompatible palladium nanoparticles for photo-based imaging and therapy. *Sci. Rep.* **2018**, *8*, 500, doi:10.1038/s41598-017-18966-8.
13. Liu, J.; He, F.; Gunn, T.M.; Zhao, D.; Roberts, C.B. Precise Seed-Mediated Growth and Size-Controlled Synthesis of Palladium Nanoparticles Using a Green Chemistry Approach. *Langmuir* **2009**, *25*, 7116–7128, doi:10.1021/la900228d.
14. Wang, Y.; Du, M.; Xu, J.; Yang, P.; Du, Y. Size-Controlled Synthesis of Palladium Nanoparticles. *J. Dispers. Sci. Technol.* **2008**, *29*, 891–894, doi:10.1080/01932690701783499.
15. Coronado, E.; Ribera, A.; García-Martínez, J.; Linares, N.; Liz-Marzán, L.M. Synthesis, characterization and magnetism of monodispersed water soluble palladium nanoparticles. *J. Mater. Chem.* **2008**, *18*, 5682–5688, doi:10.1039/B811190A.
16. Castellanos-Rubio, I.; Insausti, M.; Gil de Muro, I.; Rojo, T.; Lezama, L. Tuning the Size of Palladium Nanoparticles in Organic and Aqueous Solutions: Influence of Aminated and Thiolated Ligands. *J. Nanosci. Nanotechnol.* **2016**, *16*, 4071–4079, doi:10.1166/jnn.2016.11711.
17. Piao, Y.; Jang, Y.; Shokouhimehr, M.; Lee, I.S.; Hyeon, T. Facile Aqueous-Phase Synthesis of Uniform Palladium Nanoparticles of Various Shapes and Sizes. *Small* **2007**, *3*, 255–260, doi:10.1002/smll.200600402.
18. Kim, S.-W.; Park, J.; Jang, Y.; Chung, Y.; Hwang, S.; Hyeon, T.; Kim, Y.W. Synthesis of Monodisperse Palladium Nanoparticles. *Nano Lett.* **2003**, *3*, 1289–1291, doi:10.1021/nl0343405.
19. Yang, Z.; Klabunde, K.J. Synthesis of nearly monodisperse palladium (Pd) nanoparticles by using oleylamine and trioctylphosphine mixed ligands. *J. Organomet. Chem.* **2009**, *694*, 1016–1021, doi:10.1016/j.jorganchem.2008.11.030.
20. Teranishi, T.; Miyake, M. Size Control of Palladium Nanoparticles and Their Crystal Structures. *Chem. Mater.* **1998**, *10*, 594–600, doi:10.1021/cm9705808.