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Size-controlled electrochemical synthesis of palladium nanoparticles using morpholinium ionic liquid

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Abstract−We have successfully synthesized morpholinium ionic liquid-stabilized palladium (Pd) nanoparticles by electrochemical reduction. For characterization of Pd nanoparticles, FT-IR, UV-visible spectroscopy, and Transmission electron microscopy (TEM) were employed. The FT-IR spectrum of Pd nanoparticles indicated the surface binding of the IL to the nanoparticles. The UV-visible spectrum showed that nano-sized Pd particles were produced. The particle size was controlled by the adjustment of the current density, temperature, and electrolysis duration. The TEM images showed an average size of 2.0, 2.2, 2.4, 2.9, 3.5, 3.9, and 4.5 nm. Nearly a 0.5 nm-sized control of the nanoparticle was achieved. The particle size increased with a decrease in the current density and an increase in temperature and electrolysis duration. The electron diffraction patterns of resulting nanoparticles indicated that the particles had a crystalline structure.

Key words: Ionic Liquid, Morpholinium Salt, Palladium Nanoparticles, Electrochemical Synthesis, Size Control

INTRODUCTION

Metal nanoparticles have unusual optical, electrical, and chemical properties, which can lead to new advanced materials in chemical sensors, optical materials, and electronic devices. To these possible applications, it is essential to develop effective methods to synthesize the nanoparticles with well-controlled size because their properties greatly depend on size [1]. In a chemical reduction method, generally, their sizes are controlled by varying the concentration of precursor and the carbon-chain length of protective agent, and a kind of reductant. The enhancement of product reproducibility has, however, remained as a challenging research task. Alternatively, the electrochemical reduction method developed by Reetz et al. showed that highly size-selective nanoparticles were produced by an adjustment of the current density [2]. This method has been proven to have some advantages over the chemical reduction method: the particle size can be tuned through an easy operation by varying the current density and electrolysis duration [3], and it is possible to obtain boride-free nanoparticles due to the lack of a requirement for a reductant such as $NaBH_4$. However, the poor electrochemical stability of the ammonium salts that are widely employed in the electrochemical synthesis remains problematic [4].

Ionic liquids (ILs) have received growing attention in green industrial applications owing to their favorable properties to be an alternative to traditional organic solvents [5]. They are normally stable in air and water, and have low melting points, sometimes as low as −96 °C [6]. Moreover, various miscibilities with water or organic solvents are easily tuned by the anion conformation. Based on these features of ILs, recently, the number of reports on ILs for the synthesis of metal or inorganic nanostructures has been gradually increasing [7,8].

In our recent reports, we developed a new synthesis of metal nanoparticles using thiol-functionalized ionic liquids (TFILs) [8]. Although the previously proposed method has many advantages, it is still problematic in that the complex synthesis route of TFILs causes a decrease in the reproducibility of the IL synthesis, which also results in the low reproducibility of nanoparticles. In this context, we synthesized N-butyl-N-methyl-morpholinium tetrafluoroborate [$Mor_{1,4}$][BF_4]. The synthesis and purification procedures for the morpholinium IL are much simpler than those for the TFILs, and the cost of the raw material is cheaper than that of imidazolium and ammonium salts. Furthermore, the electrochemical stability of morpholinium IL is much better than that of the ammonium salt [5a]. With these desirable features, in this study, we describe the preparation of [$Mor_{1,4}$][BF_4]-stabilized Pd nanoparticles based on the electrochemical reductions, and synthesize the nanoparticles with fine-tuned sizes by varying the current density, temperature, and electrolysis duration.

EXPERIMENTAL SECTION

1. Materials

4-methylmorpholine (Aldrich, 99%), 1-bromobutane (Aldrich, 99%), sodium tetrafluoroborate (Aldrich, 98%), palladium foil (Alfa Aesar, 99.9%), and platinum foil (Nilaco, 99%) were used without other treatments. Acetonitrile (99.9%), acetone (99.9%), and ethanol (99.9%) were obtained from Merck and used as received.

2. Preparation

2-1. Preparation of Morpholinium Ionic Liquid

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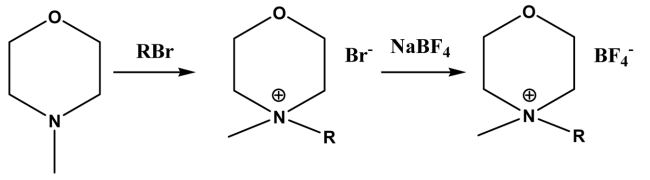

Scheme 1. Synthetic procedure of N-butyl-N-methyl-morpholinium tetrafluoroborate [$Mor_{1,4}$][BF_4].

Table 1. Summary of preparative results of Pd nanoparticles

Sample	Current density	Temperature	Electrolysis duration	Particle size
1	1.11 mA/cm^2	23 ℃	180.4 C	2.4±0.3 nm
2	0.74 mA/cm^2	23 ℃	180.4 C	2.9±0.3 nm
3	0.37 mA/cm^2	23 ℃	180.4 C	3.5±0.5 nm
4	0.19 mA/cm^2	23 ℃	180.4 C	3.9±0.6 nm
5	1.11 mA/cm^2	13 ℃	180.4 C	2.2±0.3 nm
6	1.11 mA/cm^2	31 ℃	180.4 C	4.5±0.9 nm
7	1.11 mA/cm^2	23 ℃	27.5 C	2.0±0.1 nm

Scheme 1 shows the synthetic procedure of [$Mor_{1,4}$][BF_4] used in this study. The synthetic procedure was divided into two steps. The desired cation was formed and then the bromide anion was converted into the corresponding BF_4^- by a metathesis reaction. The detailed synthetic procedure was as follows.

4-Methylmorpholine (0.30 mol) was reacted with an excess of bromobutane in a round-bottom flask in a nitrogen atmosphere, by using 200 mL of acetonitrile as solvent, to produce N-butyl-N-methylmorpholinium bromide [$Mor_{1,4}$][Br]. The mixture was refluxed for 5 hours at 70 ℃. The white crystalline solid ([$Mor_{1,4}$][Br]) was obtained by recrystallization at room temperature with acetone (yield 82.00%). Then, [$Mor_{1,4}$][Br] (0.20 mol) was reacted with sodium tetrafluoroborate (0.20 mol) in acetone (25 ℃, 24 hours), and [$Mor_{1,4}$][BF_4] was formed. Sodium bromide was removed by filter paper. After rotor-evaporation, the product ([$Mor_{1,4}$][BF_4]) was dried under vacuum at 50 ℃ (yield 81.70%). The ^{1}H NMR and FAB mass spectra were recorded on a Bruker DMX 600 MHz NMR spectrometer and FAB mass JMS-HX110A, respectively. The possible presence of residual Br^- was examined by ionic chromatography (System: Bio-LC DX-300 (Dionex, Sunny-vale, CA, USA); detector: suppressed conductivity (PED2); column: ICSep AN300 with ICSep ANSC guard). ^{1}H-NMR (Acetone, δ/ppm, relative to TMS) 4.12-4.03 (4H), 3.67-3.60 (6H), 3.36 (3H), 1.92-1.85 (2H), 1.48-1.40 (2H), 1.00-0.97 (3H). FAB MS: m/z=158 [$Mor_{1,4}$]$^+$. Br-content: 145 ppm.

2-2. Preparation of Pd Nanoparticles

The electrochemical preparation of Pd nanoparticles was performed in a simple two-electrode cell by using a Solartron 1260A potentiostat/galvanostat at 23 ℃. A 1.8 cm×1.5 cm palladium foil and a 2.0 cm×2.2 cm platinum foil were used as the anode and cathode, respectively, and were placed 5 mm apart. [$Mor_{1,4}$][BF_4] in acetonitrile (6.67 mM) served as both a supporting electrolyte and stabilizer. The applied current density was 1.11 mA/cm^2, and elec-

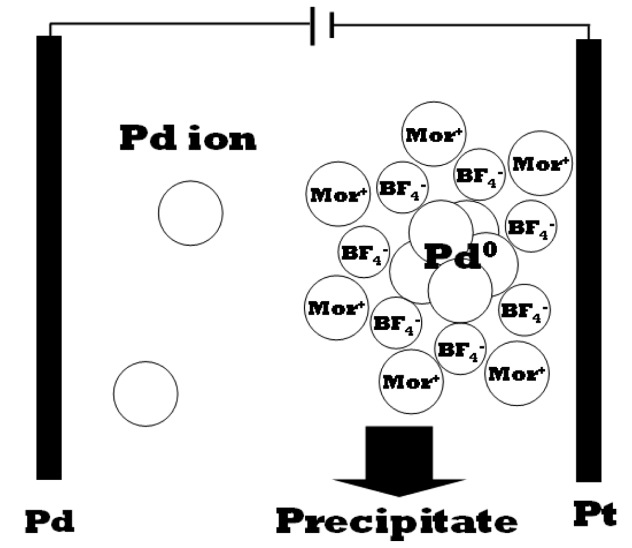

Fig. 1. Representation of electrochemical formation of the IL-stabilized Pd nanoparticles.

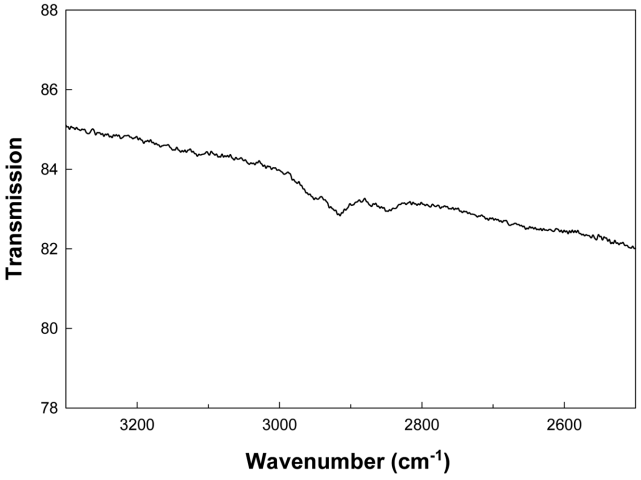

Fig. 2. FT-IR spectrum of purified Pd nanoparticles (Sample 1).

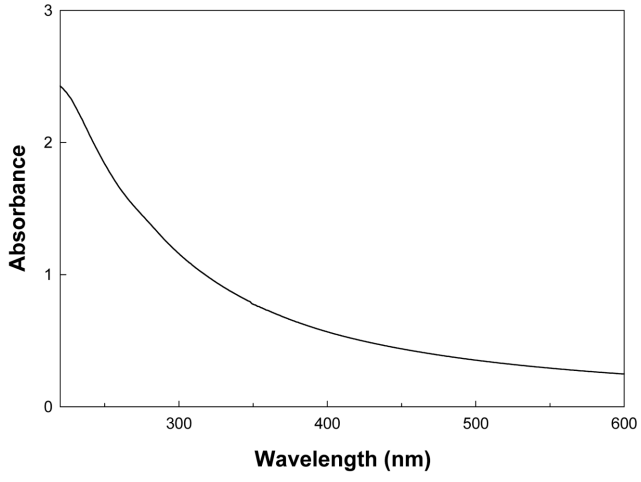

Fig. 3. UV-visible spectrum recorded from Pd colloidal suspension after electrolysis (Sample 1).

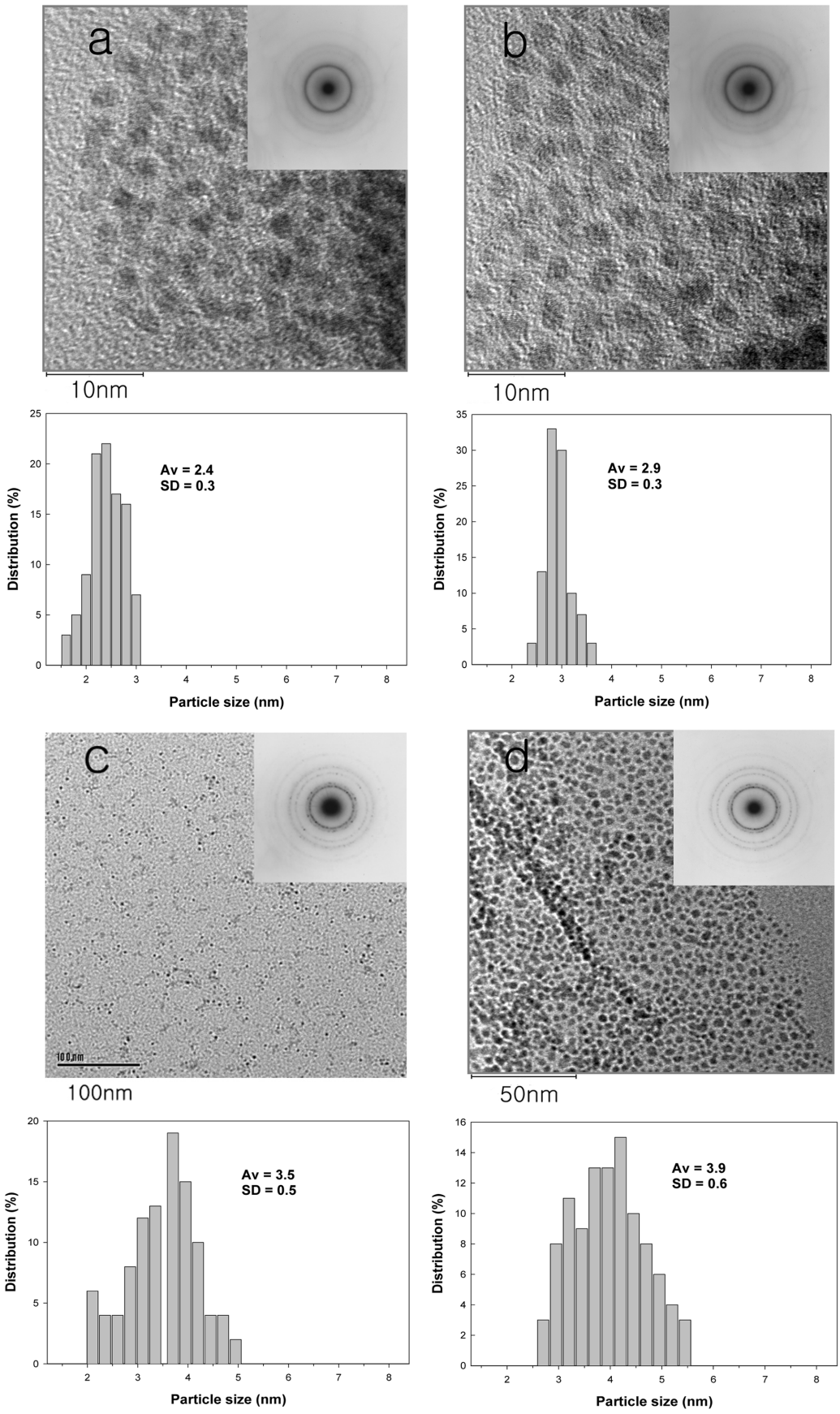

Fig. 4. TEM images, electron diffraction patterns (inset), and size distribution diagrams for Pd nanoparticles with various current densities: (a) 1.11 mA/cm^2 (Sample 1); (b) 0.74 mA/cm^2 (Sample 2); (c) 0.37 mA/cm^2 (Sample 3); and (d) 0.19 mA/cm^2 (Sample 4).

trolysis was carried out until 180.4C was reached. The other samples listed in Table 1 were prepared in a similar way by changing the current density, temperature, and electrolysis duration. The resulting nanoparticles were purified by the removal of unbound IL with ethanol and were then centrifuged.

3. Characterization

Transmission electron microscopic (TEM) images and electron diffraction patterns were obtained from a Phillips TECHNAI F-20 at beam energy of 200 kV. Sample grids were prepared as in the following procedure. The nanoparticles were redispersed in tetrahydrofuran (THF) and one droplet of the solution was placed on a 300 mesh carbon-coated copper grid. Then, the solvent was evaporated under ambient condition. The ATR-FTIR spectra of Pd nanoparticles and UV-visible absorption spectra of colloidal dispersions after electrolysis were recorded on a TravelIR Portable and a Varian CARY 100 conc, respectively.

RESULTS AND DISCUSSION

$[Mor_{1,4}][BF_4]$-stabilized Pd nanoparticles were prepared by electrochemical reductions with various current densities, temperatures and electrolysis durations. Fig. 1 schematically illustrates the electrochemical formation of IL-stabilized Pd nanoparticles. Pd ions released from the Pd anode migrated to the Pt cathode and then Pd ions were reduced to Pd ad-atoms. Subsequently, Pd ad-atoms were stabilized by the IL, which prevents Pd atoms from agglomeration [9] and leads to nanoparticle formation. The resulting nanoparticles accumulated on the bottom of cell. In this process, the larger potential window of the IL makes the IL serve as both effective stabilizer and supporting electrolyte [10].

The purified nanoparticles show C-H aliphatic vibrations at near 2,900 cm^{-1} in the FT-IR spectrum (Fig. 2). The result demonstrates that Pd particles coexist with the IL and the IL might be bound to the surface of particles [11]. The formation of nano-sized Pd particles was confirmed by the UV-visible absorption spectrum. The absorption spectrum of Sample 1 in the organic phase is shown in Fig. 3. There is no obvious surface plasmon band and the spectrum consists of a smoothly increasing absorption at increasing energy. This is typical of nano-meter sized Pd particles [12]. Other samples also show the similar UV-visible absorption spectra with Fig. 3.

The average size of the Pd nanoparticles was investigated by TEM.

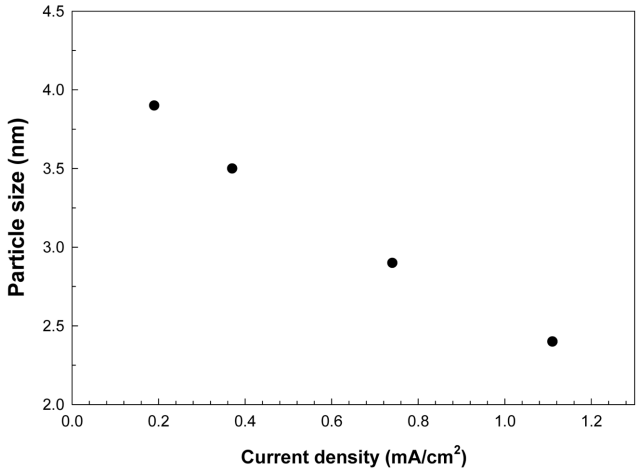

Fig. 5. Effect of the current density on Pd nanoparticle size (electrolysis duration=180.4 C, T=23 ºC).

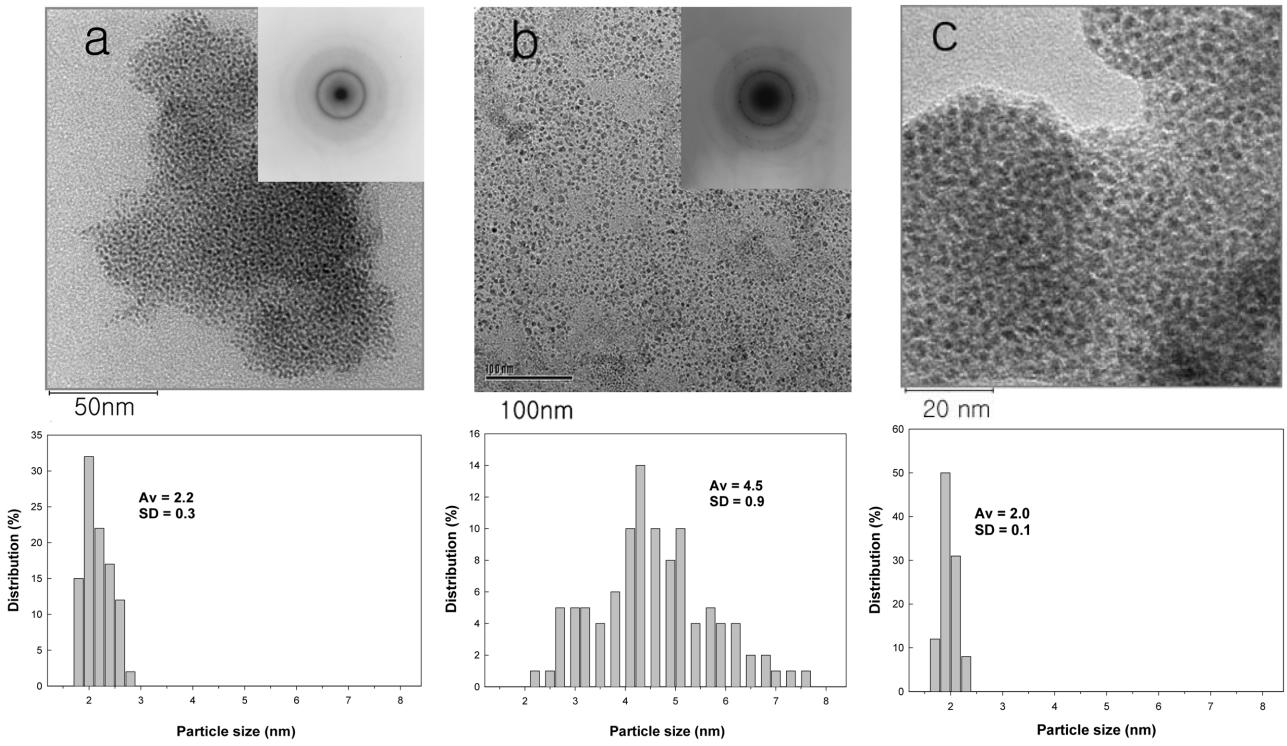

Fig. 6. TEM images, electron diffraction patterns (inset), and size distribution diagrams: (a) Pd nanoparticles prepared at 13 ºC (Sample 5); (b) 31 ºC (Sample 6); and (c) Pd nanoparticles with electrolysis duration of 27.5 C (Sample 7).

In the electrochemical preparation, the particle size is strongly influenced by the current density [2], because the reduction rate of Pd ions to Pd ad-atoms is proportional to the current density. To examine this effect on the particle size, $[Mor_{1,4}][BF_4]$-stabilized Pd nanoparticles were prepared by the variation of the current density. The TEM images shown in Fig. 4 indicate that the average sizes are 2.4, 2.9, 3.5, and 3.9 nm for Samples 1, 2, 3, and 4, respectively. Interestingly, the particle size linearly decreases with increasing the current density (Fig. 5). This result can be explained with the mechanism of particle formation. That is, it is known that the competition between the nucleation and growth of particles determines the average size. In electrochemical synthesis, the fast reduction rate of Pd ions as a result of the high current density produces more Pd nuclei and suppresses the growth of Pd nanoparticles. Therefore, the diameter of the resulting Pd nanoparticles at a higher current density becomes smaller. In addition, the selected area electron diffraction (SAED) patterns of Samples 1, 2, 3, and 4 reveal that they are crystalline with face-centered cubic packing arrangements of bulk metals.

Temperature appears to be also a decisive parameter for determining the particle size. Preparations at 13 ºC and 31 ºC (Samples 5 and 6) afford Pd nanoparticles with the average size of 2.2 and 4.5 nm, respectively (Figs. 6a, 6b). Thus, the particle size becomes smaller in the order of 13, 23, and 32 ºC, which is shown in Fig. 7. This result is because the crystal growth is slow at a low temperature. The SAED patterns show that the prepared particles are crystalline structures. Subsequently, we prepared Pd nanoparticles with the electrolysis duration of 27.5C, in order to investigate the possible effect of electrolysis duration on the particle size. Fig. 6c shows that the average size and standard deviation of Sample 7 with electrolysis duration of 27.5C are 2.0 nm and 0.1 nm, respectively. The obtained particles indicate that the average size is smaller than that of the particles with electrolysis duration of 180.4C (Sample 1), which suggests that although precipitation is observed at initial time for the electrolysis, further growth of the particles occurs during the electrolysis. However, another possible explanation for larger particles formed at longer electrolysis duration has been also suggested. That is, decreasing the concentration of stabilizer during the electrolysis results in insufficient protection of metal nanoparticles, leading to the formation of larger particles [3].

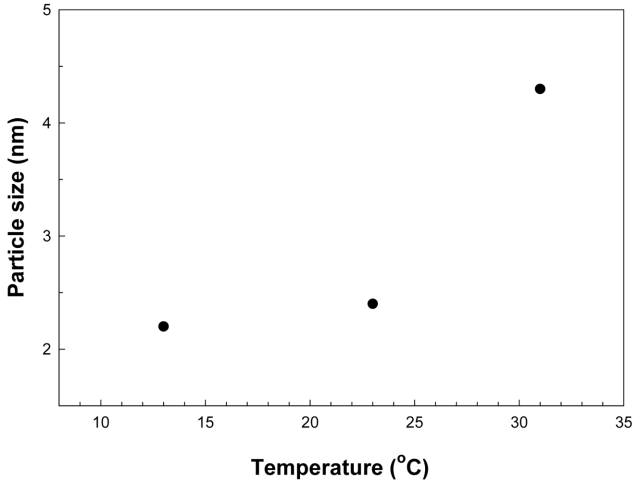

Fig. 7. Effect of the temperature on Pd nanoparticle size (current density=1.11 mA/cm^2, electrolysis duration=180.4 C).

Various synthetic procedures for the size-selective nanoparticles have been intensively studied based on the chemical reduction, but no other results have led to the fine size control of Pd nanoparticles as in this work. In the electrochemical method, furthermore, the control of monodispersity can be easily attained by the adjustment of various parameters [3]. These features make the proposed method promising for the synthesis of near monodisperse nanoparticles with well-controlled sizes.

CONCLUSION

We have successfully synthesized Pd nanoparticles by electrochemical reduction. The IL served as both an effective stabilizer and a supporting electrolyte. As a result, nearly a 0.5 nm-sized control of the nanoparticle was achieved by the adjustment of the current density, temperature and electrolysis duration. The resulting nanoparticles showed sizes of 2.0, 2.2, 2.4, 2.9, 3.5, 3.9, and 4.5 nm. The particle size increased with decreasing the current density and increasing the temperature and electrolysis duration. Unlike in the chemical process, the electrochemical process features an easy operation for controlling the particle size. This advantage is expected to lead to enhancement in the reproducibility of nanoparticle synthesis. In addition, the better electrochemical stability of ILs will allow them to be applied to the electrochemical synthesis of various nano-materials.

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