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Aqueous-phase synthesis of metal nanoparticles using phosphates as stabilizers

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Abstract−We describe a simple, aqueous-phase route to the synthesis of metal nanoparticles including Pt, Pd, Ru, and Au based on the aqueous-phase reduction of metal salts with $NaBH_4$. In this approach, various phosphates were applied as new type of stabilizers for the synthesis of metal nanoparticles thanks to its negatively charged functional group (PO^-).

Keywords: Nanoparticle, Platinum, Palladium, Ruthenium, Phosphate

INTRODUCTION

Noble metal nanoparticles including platinum (Pt), palladium (Pd), ruthenium (Ru), and gold (Au) have attracted tremendous attention for their unusual catalytic properties and biocompatibility in many applications [1-11]. These nano-sized materials provide a great opportunity to take a high surface-to-volume ratio and thus improve the metal utilization in noble metal-based catalysts or electrocatalysts. In a typical catalytic reaction, the relationship between reactant and surface of catalyst is very important for obtaining high catalytic activity. To date, specific organic capping agents or polymer stabilizers have been exploited to restrict growth of nanoparticles by stabilizing their high-energy surfaces as well as to prevent agglomeration by giving nanoparticles organic layers on their surface [12-15]. Although the organic layers on the surface of nanoparticles are necessary for stabilization of nanoparticles, they often hamper the interaction between reactants and active metal sites, inhibiting catalytic activity [16-18]. Furthermore, because of their strong binding to the surface of metal nanoparticles, it is difficult to completely remove these organic molecules [18], which hinders the various practical applications in catalysis. From this point of view, the development of a synthetic route for metal nanoparticles having relatively “clean” surface can be a significant challenge to preserve catalytically active site on the surface of nanoparticles [19-21].

We report a simple aqueous-phase route to the synthesis of metal nanoparticles including Pt, Pd, Ru, and Au by reducing metal salt with $NaBH_4$ in the presence of phosphates as stabilizers. In this approach, phosphate ions can act as new type of stabilizer thanks to their negatively charged functional group (PO^-). In addition, the morphology of the metal nanoparticles could be easily controlled by using different kinds of phosphates, such as disodium phosphate (Na_2HPO_4), disodium pyrophosphate ($Na_2H_2P_2O_7$), tetrasodium pyrophosphate ($Na_4P_2O_7$), and trisodium tripolyphosphate ($Na_3P_3O_{10}$).

EXPERIMENTAL SECTION

1. Materials

Disodium phosphate (Na_2HPO_4), disodium pyrophosphate ($Na_2H_2P_2O_7$), tetrasodium pyrophosphate ($Na_4P_2O_7$), trisodium polyphosphate ($Na_3P_3O_{10}$), sodium borohydride ($NaBH_4$), potassium tetrachloroplatinate(II) (K_2PtCl_4), sodium tetrachloropalladtae(II) (Na_2PdCl_4), ruthenium(III) chloride ($RuCl_3$), and gold(III) chloride ($HAuCl_4$) were purchased from Aldrich and used without further purification.

2. Synthesis of Metal Nanoparticles

To obtain phosphate-stabilized metal nanoparticles, 0.05 mmol of phosphates (Na_2HPO_4, $Na_2H_2P_2O_7$, $Na_4P_2O_7$, and $Na_3P_3O_{10}$, Aldrich) was dissolved in deionized water (5 mL) and heated to 95 °C in air under magnetic stirring. Meanwhile, $NaBH_4$ (0.4 mg, Aldrich) was dissolved in 1 mL of deionized water at room temperature. The aqueous $NaBH_4$ solution was then added to the phosphate solution with a pipette. After 1.5 min, 1 mL of 5 mM metal salt aqueous solution was added and the reaction mixture was heated at 95 °C in air for 2 h, and then cooled to room temperature. The product was collected by centrifugation and washed with ethanol to remove excess reagent. The synthesized nanoparticles were well dispersed in water. Metal salts were K_2PtCl_4 for Pt, Na_2PdCl_4 for Pd, $RuCl_3$ for Ru, and $HAuCl_4$ for Au nanoparticles, respectively.

3. Characterization

Transmission electron microscopy (TEM) studies were done with an FEI Tecnai G2 Spirit microscope operated at 120 kV by drop casting the sample dispersions on carbon-coated copper grids. High-resolution TEM analyses were performed by using a JEOL 2100F microscope operated at 200 kV accelerating voltage. Powder X-ray diffraction pattern was obtained with a Rigaku D-MAX/A diffractometer at 35 kV and 35 mA. Fourier transform infrared spectros-

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[‡] This article is dedication to Prof. Sung Hyun Kim on the occasion of his retirement from Korea University.

copy (FT-IR) analysis was performed using a Jasco FTIR-6100 equipped with ATR assembly in the transmission mode.

RESULTS AND DISCUSSION

Fig. 1(a) shows a TEM image of Pt nanoparticles synthesized using monatomic phosphate (Na_2HPO_4) as a stabilizer. Most of the as-synthesized Pt nanoparticles exhibited a spherical profile with an average size of 3.0 nm. HRTEM image in Fig. 1(a) shows that the Pt nanoparticles had a single-crystalline structure. The fringe with a lattice spacing of 2.23 Å can be indexed as {111} of face-centered cubic (fcc) Pt. The powder XRD pattern of the product (Fig. 1(b)) was well matched with that of fcc Pt (*Fm3m*, a=3.88 Å, Joint Committee on Powder Diffraction Standards (JCPDS) file No. 87-0647), confirming the formation of metallic Pt nanoparticles. The FT-IR spectrum of the Pt nanoparticles showed three distinct peaks at around 900, 1,100, and 1,500 cm^{-1} (Fig. 1(c)), which can be attributed to stretching vibration of a P-O-H single bond [22].

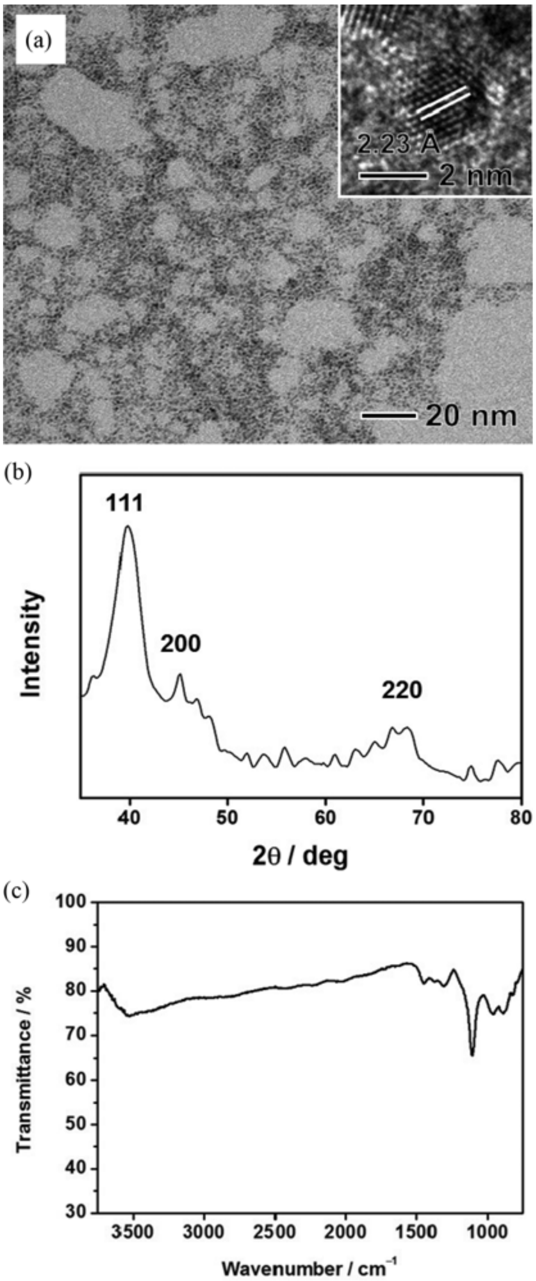

Fig. 1. (a) TEM and HRTEM (inset) images, (b) XRD pattern, and (c) FT-IR spectrum of the Pt nanoparticles synthesized by reducing K_2PtCl_4 with $NaBH_4$ in the presence of Na_2HPO_4 as a stabilizer.

In the present synthesis, Na_2HPO_4 is believed to play a critical role in the formation and stabilization of Pt nanoparticles in an aqueous phase. When the synthesis was conducted in the absence of Na_2HPO_4, black precipitates were formed, showing that product was not stable in an aqueous phase. Previous studies based on Derjaguin-Landau-Verwey-Overbeek (DLVO) theory showed that nanoparticle dispersions can be stabilized by electrostatic and/or steric interactions [23]. In our work, since the Na_2HPO_4 has negatively charged functional groups (PO^-) and a short molecular length (less than 1 nm), it is not unreasonable to assume that the electrostatic repulsion would be a major force for the stabilization of Pt nanoparticles in an aqueous phase. The zeta potential value of the Pt nanoparticles was around −30.0 mV, showing the presence of the elec-

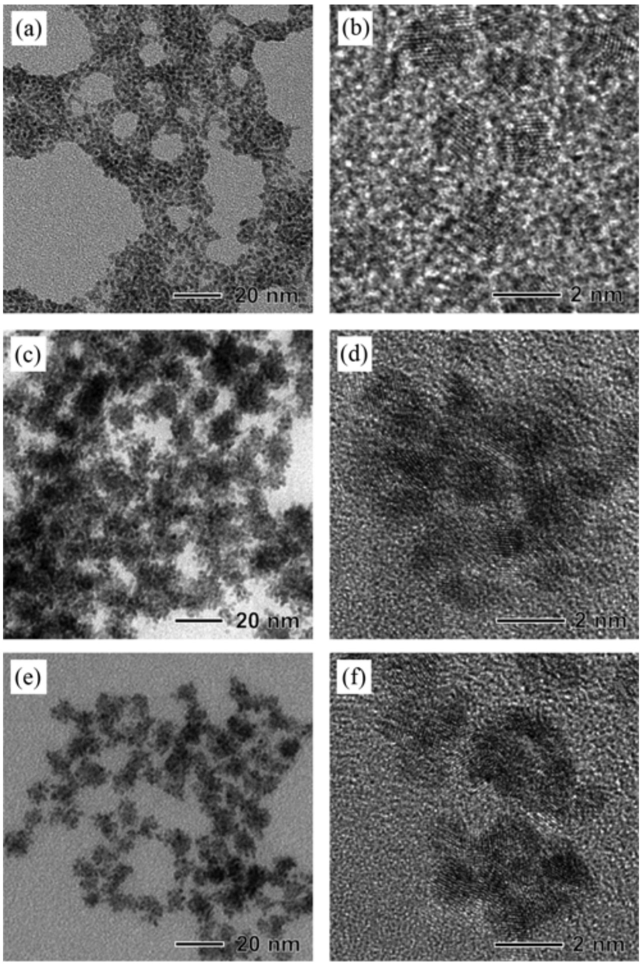

Fig. 2. TEM and HRTEM images of Pt nanoparticles synthesized using various phosphates as stabilizers: (a), (b) $Na_2H_2P_2O_7$, (c), (d) $Na_4P_2O_7$, and (e), (f) $Na_3P_3O_{10}$.

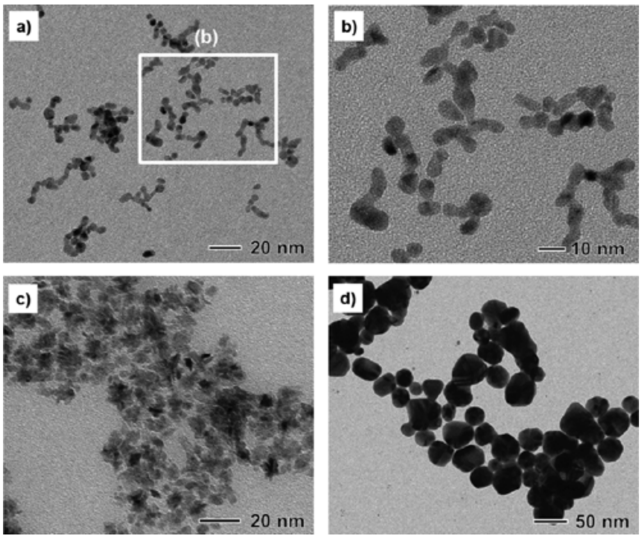

Fig. 3. TEM images of (a), (b) Pd, (c) Ru, and (d) Au nanoparticles, respectively.

trostatic stabilization by the negatively charged nanoparticles.

The morphology of Pt nanoparticles can be easily controlled by introducing various kinds of phosphates. When the synthesis was conducted in the presence of $Na_2H_2P_2O_7$ instead of Na_2HPO_4, Pt nanoparticles with sizes of around 3.5 nm were synthesized (Fig. 2(a) and (b)). However, 20 nm-sized aggregates composed by 14-16 number of 3 nm-sized Pt nanoparticles were observed when the synthesis was conducted using $Na_4P_2O_7$ as a stabilizer (Fig. 2(c) and (d)). Even though $Na_2H_2P_2O_7$ and $Na_4P_2O_7$ are both diatomic phosphates, $Na_2H_2P_2O_7$ has two negatively charged (O^-) functional groups, while $Na_4P_2O_7$ has four groups. We believe that $Na_4P_2O_7$ would act as a linker to connect the synthesized Pt nanoparticles, thus leading to the formation of aggregate structures. When we used $Na_3P_3O_{10}$, which has large number of negatively charged functional groups, aggregates were also observed in the TEM image, confirming the role of polyatomic phosphates (Fig. 2(e) and (f)).

The current synthetic method turned out to be extensively applicable, and we could successfully synthesize other noble metal nanoparticles. For example, when the Na_2PdCl_4 was used as a precursor while keeping the other experimental conditions unchanged, worm-like structures composed of a few number of 5 nm-sized Pd nanoparticles were synthesized (Fig. 3(a)). Fig. 3(b) shows that small Pd nanoparticles were connected with each other and formed branched and polycrystalline structures. Ru nanoparticles with irregular shapes were also synthesized by using $RuCl_3$ instead of K_2PtCl_4 as a precursor (Fig. 3(c)). The size of polycrystalline Ru nanoparticles was around 5-20 nm. Morphology and size of Au nanoparticles synthesized using $HAuCl_4$ as a precursor were spherical and around 50 nm, respectively (Fig. 3(d)). These results indicate that kinds of metal would be important for the size and morphology of the nanoparticles.

CONCLUSIONS

We have demonstrated a simple aqueous-phase route to the synthesis of metal nanoparticles with controllable morphologies by introducing phosphates as stabilizers. The size and morphology of Pt nanoparticles were easily controlled by using different kinds of phosphates such as Na_2HPO_4, $Na_2H_2P_2O_7$, $Na_4P_2O_7$, and $Na_3P_3O_{10}$. In addition, we could also extend this synthetic method to other metal nanoparticles, for example, Pd, Ru, and Au.

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