

Synthesis of Pd–Pt–P amorphous nanoparticles

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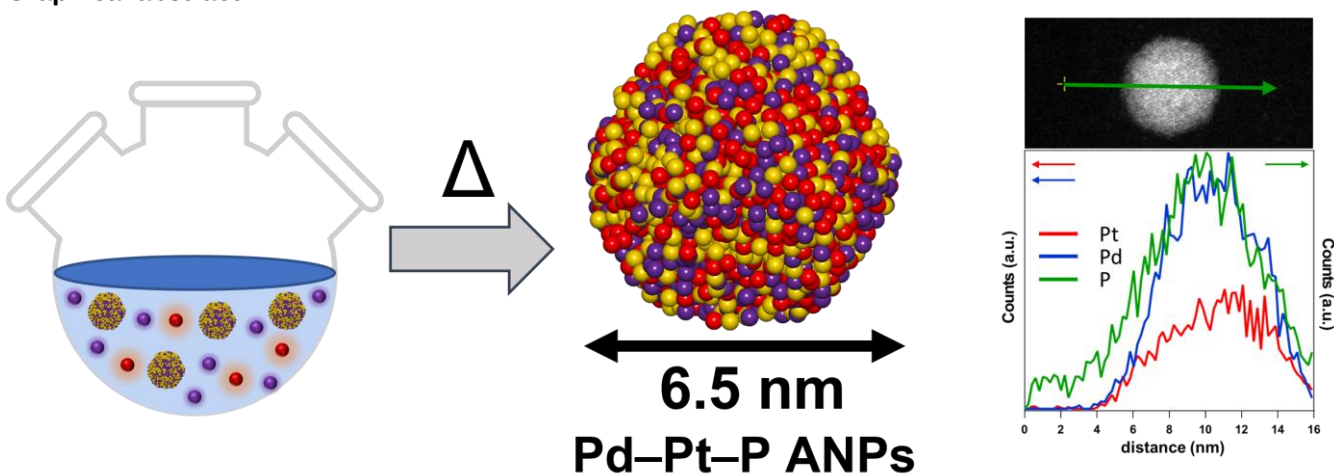
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Abstract

Amorphous materials are very attractive materials because of their unique properties, including high corrosion resistance and catalytic activity. Creating such materials on a nanoscale is very effective in maximizing their performance. However, it is difficult to synthesize amorphous nanomaterials by conventional rapid cooling methods, commonly used for bulk amorphous materials. Therefore, there are not as many reports about amorphous nanomaterials as bulk materials. Herein we report the first synthesis of Pd–Pt–P amorphous nanoparticles by a two-step synthesis method. They were also characterized.

Keywords: synthesis, amorphous, nanomaterial

Graphical abstract



1 The physical and chemical properties of inorganic
2 materials can be controlled by various features such
3 as size,¹ atomic arrangement,^{2,3} and composition.⁴
4 Among them, atomic arrangement is one of the most
5 dominant factors. For example, it has been
6 demonstrated that catalytic properties are controlled
7 by changing the crystal structure.² Although different
8 crystal structures provide different atomic
9 arrangements, the variation is rather limited. On the
10 other hand, amorphous materials lack long-range order
11 and have a great variety of atomic arrangements.
12 Compared with crystalline materials, they have
13 complex atomic arrangements, which can give rise to
14 unique properties, including optical,⁵ magnetic,⁶ and
15 catalytic⁷ properties.

16 Platinum group metal based phosphide amorphous
17 bulk materials, in particular, have attracted much

18 attention.^{8,9} PdFeP has unique magnetic properties;¹⁰
19 PdPtP, PdRhP, and PdIrP exhibit high corrosion
20 resistance,⁸ and PdPtCuNiP exhibits high catalytic
21 activity.¹¹

22 As mentioned, the size of materials is a factor in
23 controlling their properties. Upon decreasing the size
24 of materials to nanometer order, nanomaterials exhibit
25 different properties compared with those of bulk
26 materials due to their large specific surface area or
27 their unique electronic structures. However, it is
28 challenging to synthesize amorphous nanomaterials.
29 In the conventional synthesis of amorphous materials,
30 molten bulk materials are rapidly cooled by using
31 specialized equipment.¹² Various amorphous materials
32 can be synthesized by this method; however, it is
33 difficult to apply this method to nanomaterials.

1 It is known that nanomaterials with precisely
2 controlled size can be synthesized by the wet
3 chemical reduction method. Very recently, amorphous
4 nanoparticles (ANPs) have been synthesized by this
5 method.^{13,14} In this paper, we report the first synthesis
6 of nanosized Pd-Pt-P amorphous material, Pd-Pt-P
7 ANPs, by the wet chemical reduction method.

8 Pd-Pt-P ANPs were synthesized in a two-step
9 process (see the online supplementary material for
10 more details). First, Pd-P nanoparticles (NPs) were
11 synthesized using a method modified from the
12 previous research.¹³ Second, the synthesized Pd-P
13 NPs were heated with Pt precursor in oleylamine
14 solution. The composition of the obtained sample was
15 analyzed by X-ray fluorescence spectroscopy and
16 estimated to be Pd:Pt:P = 60:17:23 (atomic ratio).

17 To confirm the structure of the synthesized material,
18 we performed powder X-ray diffraction (PXRD)
19 measurements (Fig. 1). The PXRD profile showed
20 broad peaks; it did not match with that of the typical
21 materials consisting of Pd, Pt, and P. Small and sharp
22 peaks around 29° and 45° are supposed to be
23 impurities. Presuming that the broad peak around 40°
24 corresponds to one Bragg peak from the crystalline
25 phase, the crystalline size was calculated to be $1.48 \pm$
26 0.01 nm. These results suggest that the obtained
27 material has an amorphous structure. We then used
28 transmission electron microscopy (TEM) to obtain the
29 particle size and shape (Fig. 2A). The estimated
30 particle size was 6.5 ± 1.2 nm (Supplementary
31 Information Fig. S1). This is much larger than the
32 presumed crystalline size calculated from PXRD. This
33 result indicated that the obtained NPs have
34 amorphous structure. In addition, the shape of the
35 NPs was spherical without showing facets, thus
36 supporting the amorphous nature of the obtained NPs.
37 To further support this conclusion, we performed
38 atomic resolution scanning transmission electron
39 microscopy (STEM) (HAAD-STEM: High-Angle Annular
40 Dark-Field Scanning Transmission Electron
41 Microscopy). As shown in Fig. 2B, long range order of
42 atoms was not observed, also supporting that the
43 obtained NPs are amorphous.

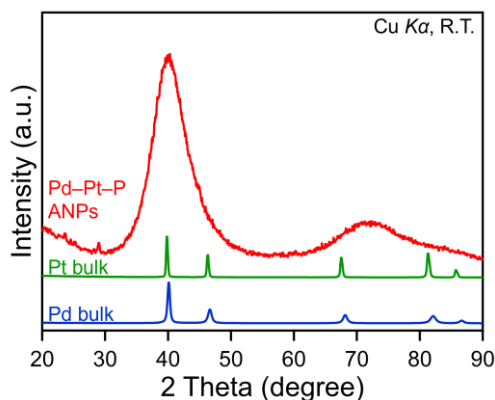


Fig. 1. PXRD profile of Pd-Pt-P ANPs.

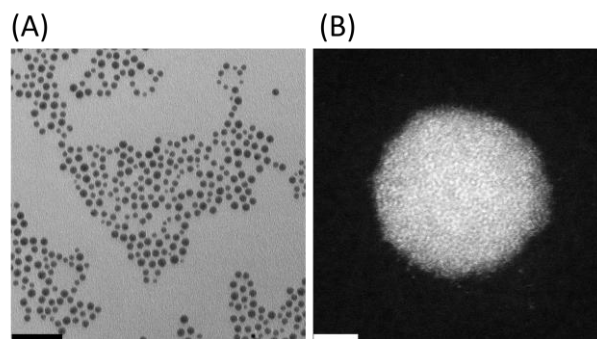


Fig. 2. (A) Typical TEM image. The scale bar is 50 nm. (B) Atomic resolution HAADF-STEM image of Pd-Pt-P ANPs. The scale bar is 2 nm.

44 To obtain further information on elemental
45 distribution, energy dispersive X-ray spectroscopy
46 (EDX) mapping was performed in STEM (Fig. 3A-C)
47 The elemental maps clearly showed that Pd and Pt are
48 homogeneously distributed in the NPs. It is difficult to
49 observe P distribution by EDX because the energy of
50 the P *K*-line and the Pt *M*-line form a spectral overlap,
51 making it difficult to deconvolute them. To obtain
52 reliable P distribution information, line scan analysis
53 was conducted using electron energy loss
54 spectroscopy (EELS) and EDX simultaneously (Fig.
55 3D-F). It was found that Pt was slightly more
56 abundant on the outside of the particles compared to
57 the Pd, but Pd, Pt, and P elements are almost
58 uniformly distributed in the ANPs (Supplementary
59 Information Fig. S2), suggesting that these three
60 elements are homogeneously mixed. These results
61 provided confirmation that solid solution Pd-Pt-P NPs
62 were successfully synthesized. P is widely distributed
63 compared to Pt and Pd. The reason will be discussed
64 later.

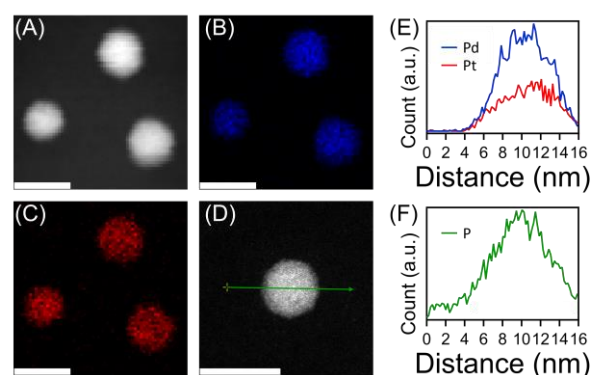


Fig. 3. STEM-EDX observation of Pd-Pt-P ANPs. (A) HAADF-STEM image. (B) Pd *K*-line, (C) Pt *L*-line. (D) The HAADF-STEM image. The green arrow shows the region of interest. Every scale bar is 10 nm (E) EDX line scan profiles of Pd (blue) and Pt (red) and (F) EELS line scan profiles of P of the ANP.

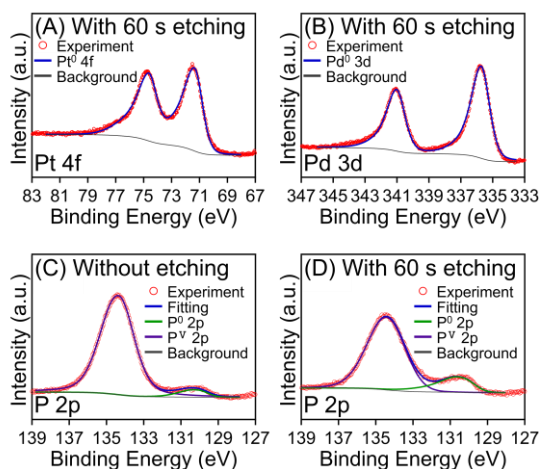


Fig. 4. XPS spectra of (A) Pt 4f with 60 s Ar etching, (B) Pd 3d with 60 s Ar etching, (C) P 2p without etching, and (D) P 2p with 60 s Ar etching.

To obtain information on the compositions and oxidation states of each element of the ANPs, we conducted X-ray photoelectron spectroscopy (XPS) analysis. XPS spectra of Pd 3d and Pt 4f (Fig. 4A,B) could be assigned to each metal component.¹⁵ The depth dependence of the Pd and Pt atomic ratio was also investigated by Ar etching. The Pd and Pt atomic ratios were calculated from peak area and ionization cross section.¹⁶ The ratios were constant, irrespective of etching time (Supplementary Information, Figs S3–S5, and Tables S1 and S2). These results suggest that Pd and Pt in ANPs are metallic and distributed throughout the ANPs. In the P 2p spectra (Fig. 4C,D and Supplementary Information, Table S3), the peaks can be deconvoluted into P⁰ and P^V peaks.^{15,17} Without Ar etching, the area of the P⁰ peak was small. However, with Ar etching, the intensity of the P⁰ peak became greater. These results indicated that P⁰ exists in ANPs. On the contrary, the intensity of the P^V peak became smaller with Ar etching. This indicates that there is a P^V component, which is presumably derived from a component formed by oxidation of tri-*n*-octylphosphine outside the ANPs.¹⁵ The binding energy of the 2p_{3/2} peak in the P⁰ component without etching and with 60 s etching shifts to –0.4 eV and –0.2 eV, respectively, with respect to that of red phosphorus (130.4 eV).¹⁸ These negative shifts in binding energy imply that the P⁰ species partially accepts electrons from the surrounding Pd and Pt.^{19,20} These suggest the formation of Pd–Pt–P alloy.

In summary, we herein report the first synthesis of Pd–Pt–P amorphous nanoparticles. These materials were characterized by PXRD, TEM, STEM equipped with EDX and EELS, and XPS. This work demonstrated the potential of a wet chemical method to synthesize amorphous nanomaterials, leading to enrichment of the library of this class of materials.

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Supplemental data

Supplementary material is available at *Chemistry Letters*

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