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Versatile Synthesis of Polyaniline/Pd Nanoparticles and Catalytic Application

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Summary: Polyaniline/Pd nanoparticles were synthesized through two approaches. "Direct reduction approach" was revealed to be a simple method to prepare small (2–7 nm) and dispersed polyaniline/Pd nanoparticles via reduction with sodium borohydride. On the other hand, "template approach" was developed to provide a versatile route to small and well-dispersed nanoparticles (1–4 nm, average diameter = 2.4 nm) with high Pd density due to pre-organization of Pd(II) species on polyaniline into the corresponding d,π-conjugated complex. Thus-obtained nanoparticles worked as an efficient redox catalyst for oxidative coupling reaction of 2,6-di-*t*-butylphenol.

Keywords: catalysts; metal-polymer complexes; nanoparticles; polyaniline

Introduction

Hybrid systems of metal nanoparticles and π-conjugated polymers or molecules have become of great interest because of their potential applicability to electronic devices, chemical sensors, and catalysts.[1] Polyaniline (PANI) is one of the most important π-conjugated compounds because of its electrical, optical, and redox properties. We have studied the synthesis of d,π-conjugated complexes of π-conjugated compounds including PANI and its derivatives with various metal salts, such as Pd(II) and Cu(II), and even heterometals (Figure 1, top right).[2–10] Furthermore, PANI was demonstrated to serve as a redox-active ligand in the transition-metal catalyzed oxidation reaction.[11,12] The present research was undertaken to synthesize metal nanoparticles through a d,π-conjugated system (Figure 1, bottom). Some reports described the preparation and characterization of PANI/metal nanohybrids, for instance, PANI/TiO_2,[13–16] PANI/Cu,[17–19] PANI/Au,[20–27] PANI/Ag,[28] and PANI/Pd.[20,29–34] PANI/Pd nanoparticles, which were synthesized by ligand exchange followed by polymerization of aniline, were used as a catalyst, as exemplified by the Suzuki-Miyaura coupling reaction.[34] However, versatile synthetic methods have to be developed for small nanometer-size PANI/Pd nanoparticles. Moreover, the catalytic application of such nanoparticles has been little investigated, especially, for carbon-carbon bond forming reactions.

We investigated two methods to prepare such metal nanoparticles. The simple synthesis is based on "direct reduction approach", in which metal ion and π-conjugated polymer are mixed and then reduced to form the metal nanoparticles (Figure 1). The other is "template approach", which involves two stages: 1) the complex formation of metal ion with the π-conjugated polymer, 2) the reductive aggregation of metallic species of the coordination complex (Figure 1).[35] In the case of the former strategy, generally, use of excess amounts of the polymer to the metal ion is necessary to prepare small and well-dispersed nanoparticles to inhibit the formation of large aggregated metal colonies. However, the second strategy is envisaged to provide small and well-dispersed nanoparticles even in a high molar ratio of metal ion/polymer because the metal species are

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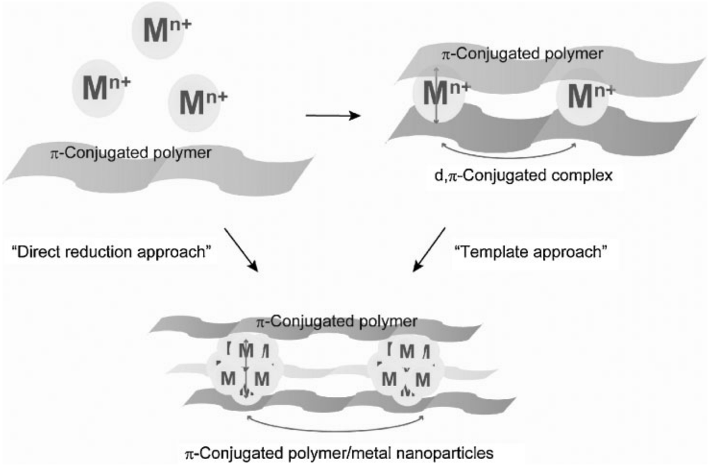


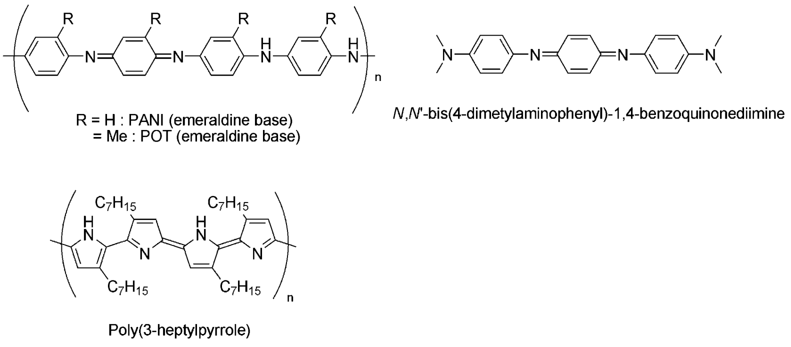
Figure 1.
Schematic representation of synthetic approaches for π-conjugated polymer/metal nanoparticles, by "direct reduction approach" and "template approach" from the d,π-conjugated complex.

pre-organized on the polymer. Herein, we describe the reductive synthesis of small dispersed Pd nanoparticles through both "direct reduction approach" and "template approach", and their catalytic activity for the oxidative coupling of 2,6-di-*t*-butylphenol.

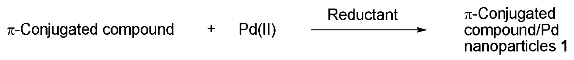
Direct Reduction Approach

We examined the chemical reduction of $PdCl_2$ in the presence of PANI, its derivatives, or polypyrrole (Scheme 1). Hydroquinone, EtOH, ascorbic acid, or sodium borohydride was employed as a reductant. Ten-time excess amounts of the π-conjugated polymer to $PdCl_2$ was employed (the molecular weight of four units of the monomer was used to calculate the molar ratio). The observed size of the particles using transmission electron microscopy (TEM) was summarized in Table 1. Hydroquinone reduced $PdCl_2$ in the

(a) π-Conjugated compounds



(b) Synthetic scheme of π-conjugated compound/Pd nanoparticles **1**



Scheme 1.
(a) π-Conjugated compounds and (b) synthetic scheme of π-conjugated compound/Pd nanoparticles **1**.

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Table 1.
The average diameter and dispersity of Pd nanoparticles.

Entry	Solvent	Reductant	Ligand	Molar ratio[a] ($PdCl_2$/ligand)	Size of diameter (nm)	Dispersity[b]
1	THF	Hydroquinone	POT	1/10	50–100	C
2	THF	N_2H_4	POT	1/10	10–100	B
3	THF	Ascorbic acid	POT	1/10	3–7	B
4	THF	EtOH	POT	1/10	3–5	C
5	THF/EtOH	$NaBH_4$	POT	1/10	2–6	A
6	THF/EtOH	$NaBH_4$	PANI	1/10	2–6	A
7	DMSO/EtOH	$NaBH_4$	PANI	1/10	2–6	A
8	NMP/EtOH	$NaBH_4$	PANI	1/10	3–7	B
9	DMF/EtOH	$NaBH_4$	PANI	1/10	3–5	B
10	THF/EtOH	$NaBH_4$	PANI	1/5	3–5	B
11	THF/EtOH	$NaBH_4$	PANI	1/30	3–5	A
12	THF/EtOH	$NaBH_4$	Polypyrole[c]	1/2.5	3–5	A
13	THF/EtOH	$NaBH_4$	Aniline trimer[d]	1/10	3–5	C

[a] The molecular weight of four units of the monomer was used to calculate the molar ratio.

[b] A: each particle was dispersed independently, B: each particle was mainly dispersed independently although some aggregates of the particles were observed, C: each particle was mainly stuck together to form the aggregates.

[c] Poly(3-heptylpyrole).

[d] *N*,*N*′-Bis(4-dimetylaminophenyl)-1,4-benzoquinonediimine.

presence of poly(*o*-toluidine) (POT, emeraldine base) to give the Pd nanoparticles with 50-100 nm diameter (entry 1). The wide range of the core size was obtained using hydrazine (10–100 nm, entry 2). The reduction with ascorbic acid (entry 3) or EtOH (entry 4) gave the nanoparticles with the size of 3–7 nm and 3–5 nm, respectively, although the individual clusters aggregated to form the second structures. The use of sodium borohydride gave the nanoparticles with the smallest diameter (2-6 nm) and the highest dispersity (entry 5). The particles were ascertained to be palladium in the EDX experiment. The specific absorptions for POT were observed in the IR spectrum (1596 cm^{-1} for the quinonediimine and 1490 cm^{-1} for the phenylenediamine). Use of PANI (emeraldine base purchased from Alfa Aesar, M_W: *ca.* 7500–15000) also led to the similar nanoparticles (entry 6) as shown in Figure 2 (2–6 nm, average diameter = 3.4 nm, standard deviation $\sigma = 0.71$, number of counted particles = 171). The image shown in Figure 2 was observed all over the grid mounted clusters **1**. The size was not

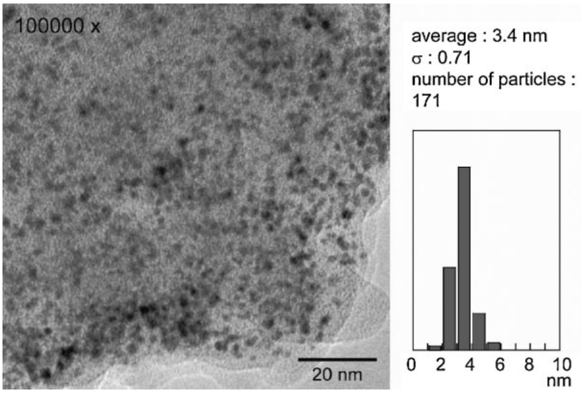
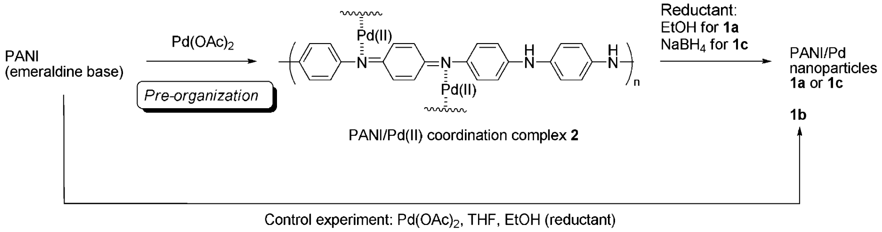


Figure 2.
TEM image of **1** prepared under the conditions of entry 6 in Table 1.



Scheme 2.
Template approach for the synthesis of PANI/Pd nanoparticles 1 and its control experiment.

strongly influenced by the solvents (entries 6, 7, 8, and 9). With regard to dispersity, THF (entry 6) and DMSO (entry 7) gave the slightly better results than NMP (entry 8) and DMF (entry 9). Finally, the molar ratio between $PdCl_2$ and PANI was changed in the range of 1/5 to 1/30 (entries 10 for 1/5 and 11 for 1/30). Some aggregates were observed in the 1/5 ratio (entry 10). As a result of optimization, the procedure using sodium borohydride in the presence of $PdCl_2$ and PANI with 1/10 ratio was confirmed with the better-reproducibility. Using this procedure, Pd nanoparticles with polypyrrole and aniline trimer were synthesized in small diameter (entries 12 and 13) although the nanoparticles with aniline trimer were aggregated under these conditions.

Template Approach

Scheme 2 shows "template approach" for the synthesis of PANI/Pd nanoparticles **1**.[35] The quinonediimine moieties of PANIs (emeraldine base) and the oligoaniline derivatives can participate to various metals in coordination, as reported in our previous study.[2,5,8–10] In the case of POT (emeraldine base), the use of $Pd(OAc)_2$ bearing two available coordination sites appeared to afford a cross-linked synthetic metal - transition metal conjugated network system.[5] To a THF solution of PANI (emeraldine base purchased from Aldrich, M_W: *ca.* 10000) was added a THF solution of $Pd(OAc)_2$ (0.67 equivalents to one quinonediimine moiety) to give the Pd(II)-coordinated PANI **2** as a solid in 87% yield. No nanoparticles were observed in the TEM analysis of **2**. The complex formation was confirmed by titration experiment using UV-vis. measurement. The red-shifted absorption appeared with decrease of the charge transfer (CT) absorption between the benzenoid and quinoid moieties of PANI due to coordination to Pd(II) (Figure 3a). This shift

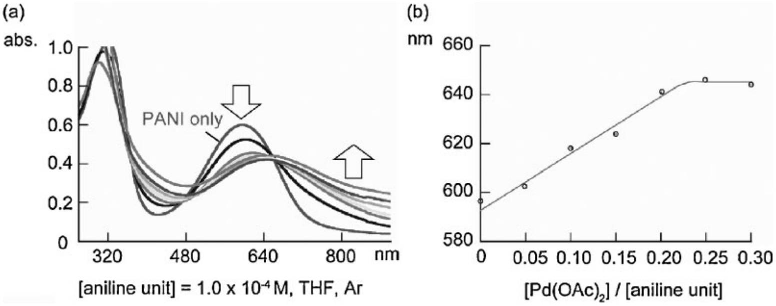


Figure 3.
The UV-vis. spectra for the complex formation of **2**, (a) the molar ratio of $Pd(OAc)_2$ on PANI (calculated based on the aniline unit) was varied as follows: 0, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3. (b) Plots of λ_{max} of CT band vs. the molar ratio of $Pd(OAc)_2$/aniline unit.

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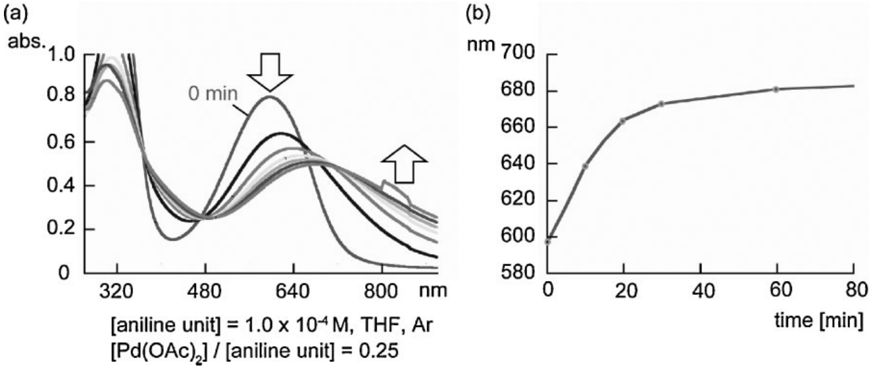

Figure 4.
The time-dependent change for the complex formation of **2**, (a) UV-vis. spectra at 0, 5, 10, 15, 20, 30, and 60 min. (b) Plots for λ_{max} of the CT band vs. time.

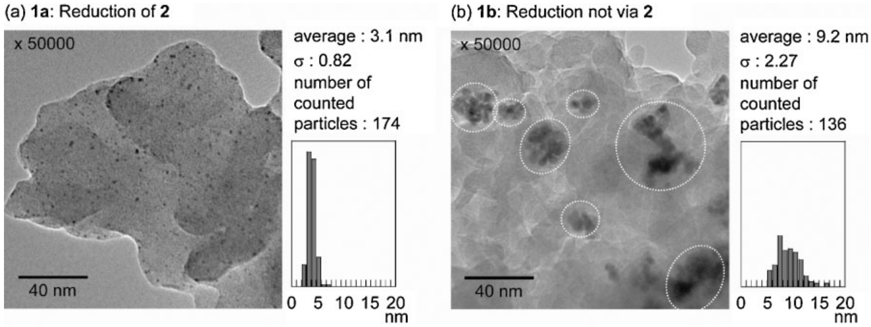

Figure 5.
TEM images and size distribution histograms of (a) **1a** and (b) **1b** prepared by reduction with EtOH.

depended on the amount of Pd(II), giving a saturation curve for complexation (Figure 3b). The time-dependent change of this experiment revealed that the complex formation completed in 1 h (Figure 4a and 4b).

The synthesis of the Pd nanoparticles was carried out by the reduction of **2**. The size of the particles was determined by TEM. First, EtOH was used as a reductant.[36] Refluxing of an EtOH solution of **2** for 1 h led to the PANI/Pd nanoparticles **1a**. The particles were ascertained to be palladium in EDX experiment. The absorptions characteristic of PANI were observed in the IR spectrum (1596 cm^{-1} for the quinonediimine and 1490 cm^{-1} for the phenylenediamine). The image shown in Figure 5a was observed all over the grid mounted clusters **1a**. The particle size of **1a** was distributed in the range of diameter 2–6 nm (average diameter = 3.1 nm, standard deviation $\sigma = 0.82$, number of counted particles = 174). In order to examine the effect of pre-organization of

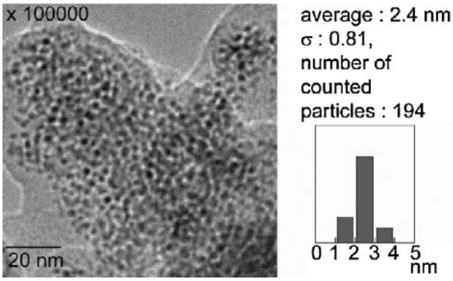

Figure 6.
TEM image and size distribution histogram of **1c** prepared by reduction of **2** with sodium borohydride.

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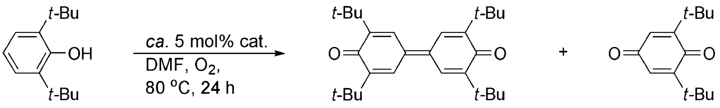
Table 2.
Oxidative coupling of 2,6-di-*t*-butylphenol.



4 **5** **6**

Entry	Catalyst	Diameter (nm)	Dispersity	Yield (%)[a]		
				4	**5**	**6**
1	PANI/Pd **1c**	1–4	Well	0	Quant	0
2	PANI/Pd **1b**	5–15	Partially aggregated	15	78	3
3	PANI	–	–	8	65	12
4	PVP/Pd[b]	2–7	Well	50	39	Trace

[a] Determined by ^{1}H-NMR with an internal standard (1,1′,2,2′-tetrabromoethane).
[b] Prepared according to reference 38.

Pd(II) species, the synthesis not via a coordination complex was also carried out (Scheme 2, control experiment). The TEM image of the thus-obtained particles **1b** is shown in Figure 5b. In contrast to the TEM image of **1a**, the aggregations were observed with **1b** (highlighted by the dotted circles in Figure 5b). Such aggregated colonies lay around in the TEM analysis of **1b**. The size of the particles **1b** was distributed in the range of diameter 5–15 nm, and the second aggregated colonies were approximately 10–50 nm by 10–50 nm (average diameter = 9.2 nm, standard deviation $\sigma = 2.27$, number of counted particles = 136). The treatment of **2** with sodium borohydride also afforded the Pd nanoparticles **1c** (average diameter = 2.4 nm, standard deviation $\sigma = 0.81$, number of counted particles = 194). The TEM image as shown in Figure 6 with the size distribution histograms was observed all over the grid mounted clusters **1c**. Notably, each particle is independent while the palladium density is high (16 wt %).[37]

Catalytic Activity

The catalytic activity for the oxidative coupling of 2,6-di-*t*-butylphenol (**4**) was investigated (Table 1). In the presence of *ca.* 5 mol% of a catalyst (based on palladium), the reaction was conducted in DMF for 24 h at 80 °C under oxygen (Table 1). The reaction with the small and well-dispersed Pd nanoparticles **1c** (1–4 nm, average diameter = 2.4 nm) gave the coupling product **5** quantitatively (entry 1). Use of the larger and aggregated nanoparticles **1b** (5–15 nm, average diameter = 9.2 nm) resulted in decrease in the yield of **5** (entry 2). In the absence of the Pd nanoparticles, **5** and the quinone **6** were obtained in 65 and 12% yields, respectively (entry 3). On the other hand, the yield was lower when the polyvinylpyrrolidone (PVP)/Pd nanoparticles[38] was used instead of PANI/Pd nanoparticles (entry 4).

Conclusion

PANI/Pd nanoparticles were synthesized through two approaches. "Direct reduction approach" is a simple method for preparing small (2–7 nm) and dispersed PANI/Pd nanoparticles via reduction with sodium borohydride. On the other hand, "template approach" provided a versatile route to small and well-dispersed nanoparticles (1–4 nm, average diameter = 2.4 nm) with high Pd density due to pre-organization of the d,π-conjugated complex. The latter method is considered to be generally applicable to other π-conjugated compound/metal nanoparticles, and even heterometallic nanoparticles. The nanoparticles showed the catalytic activity for

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oxidative coupling of 2,6-di-*t*-butylphenol (**4**) under oxygen. PANI/Pd nanoparticles are expected to serve as an efficient redox catalyst in various oxidative reactions.

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