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Template synthesis of polyaniline/Pd nanoparticle and its catalytic application

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Abstract—Pre-organization of Pd(II) species on polyaniline to form the corresponding d,π-conjugated complex provided a versatile route to a small and well-dispersed nanoparticle, which worked as an efficient redox catalyst for oxidative coupling reaction of 2,6-di-*t*-butylphenol.

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), Cu(II), and even heterometals (Fig. 1a).[2,3] Furthermore, PANI serves as a redox-active ligand in the transition-metal catalyzed oxidation reaction.[4] The present research was undertaken to synthesize a metal nanoparticle through a d,π-conjugated system (Fig. 1b). Some reports described the preparation and characterization of PANI/metal nanohybrids, for instance, PANI/TiO_2,[5] PANI/Cu,[6] PANI/Au,[7] PANI/Ag,[8] and PANI/Pd.[7a,9] PANI/Pd nanoparticle was used as a catalyst, as exemplified by the Suzuki–Miyaura coupling reaction in the presence of PANI/Pd nanoparticle with diameters of ca. 4.9 nm (the smallest so far), which is synthesized by ligand exchange followed by polymerization of aniline.[9f]

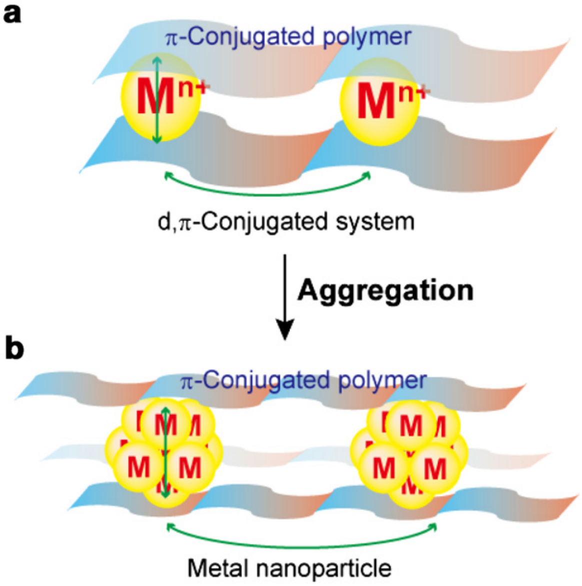

Figure 1. Schematic representation of synthetic strategy from (a) d,π-conjugated system to (b) metal nanoparticle.

Our strategy to synthesize such metal nanoparticle systems involves two stages: (1) the complex formation of metal ions with the polymer (Fig. 1a), and (2) the aggregation of the metallic species of the coordination complexes (Fig. 1b). This strategy is envisaged to provide a small and well-dispersed nanoparticle because metal ions are pre-organized on the polymer. There is no report on a strategy based on such concept in the synthesis of the hybrid systems of metal nanoparticles and π-conjugated polymers. Herein, we describe the reductive synthesis of small dispersed Pd nanoparticle **2** through template formation of PANI/Pd(II) complex **1** (Scheme 1), and its catalytic activity for oxidative coupling of 2,6-di-*t*-butylphenol.

Keywords: Nanoparticle; Catalyst; Polyaniline; Palladium.

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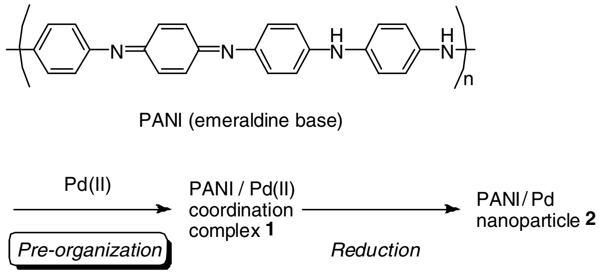


Scheme 1. Synthetic strategy for the Pd nanoparticle.

In our previous study, it was revealed that the quinonediimine moiety of PANI and oligoaniline derivatives can coordinate to Pd(II).[2,3c,f–h] To a THF solution of PANI (emeraldine base purchased from Aldrich, M_w: ca. 10,000) was added a THF solution of $Pd(OAc)_2$ (1 equiv to a quinonediimine moiety) to give the Pd(II)-coordinated PANI **1** as a solid in 87% yield.[10] No nanoparticle was observed in the transmission electron microscopy (TEM) analysis of **1**. 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) (Fig. S1). The time-dependent change of this experiment revealed that the complex formation was completed in 1 h (Fig. S2). This observation is consistent with our previous results.[3c]

The Pd nanoparticle synthesis was carried out by the reduction of **1**. The size of the particle was determined by TEM. First, ethanol was used as a reductant.[11] Refluxing of an ethanol solution of **1** for 1 h led to PANI/Pd nanoparticle **2a**. The particle was ascertained to be palladium in EDX experiment. The absorption characteristics of polyaniline was observed in the IR spectrum (1596 cm^{-1} for quinonediimine and 1490 cm^{-1} for phenylenediamine). The image shown in Figure 2a was observed all over the grid mounted cluster **2a**. The particle size of **2a** was distributed in the range of diameter 2–6 nm (average diameter = 3.1 nm, standard deviation $\sigma = 0.81$, number of counted particles = 174). In order to examine the effect of preorganization of the Pd(II) species, the synthesis not via a coordination complex was also carried out. The TEM image of the thus-obtained particle **3** is shown in Figure 2b. In contrast to the TEM image of **2a**, the aggregation was observed with **3** (highlighted by the dotted circles in Fig. 2b). Such aggregated colony lay around in the TEM analysis of **3**. The size of particle **3** was distributed in the range of diameter 5–15 nm, and the second aggregated colony was 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 **1** with $NaBH_4$ also afforded Pd nanoparticle **2b** (average diameter = 2.4 nm, standard deviation $\sigma = 0.81$, number of counted particles = 194). TEM image and size distribution histograms are shown in Figure 3.[12] The image shown in Figure 3 was observed all over the grid mounted cluster **2b**. To the best of our knowledge, the obtained PANI/Pd nanoparticle exhibits the smallest average diameter. Notably, each particle is independent while the palladium density is high (16 wt %).[13]

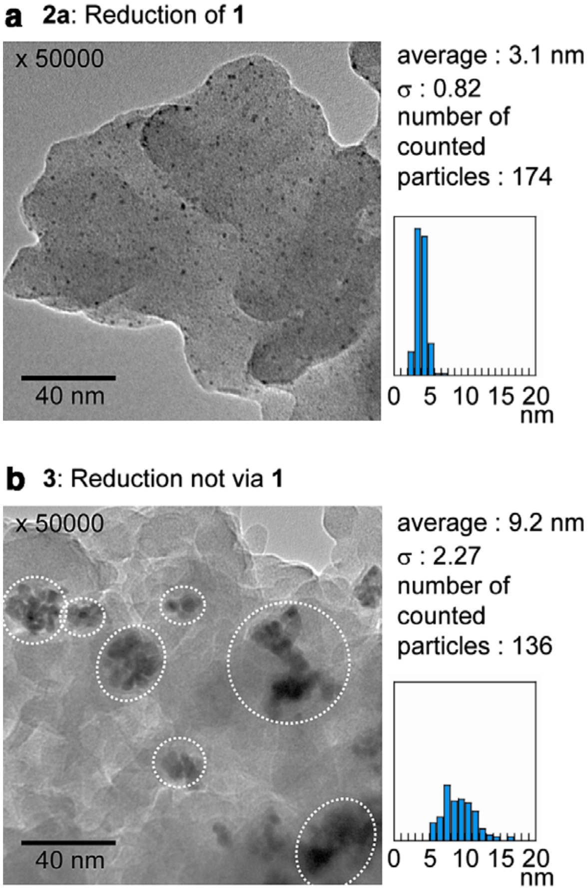


Figure 2. TEM images of (a) **2a** and (b) **3** prepared by the reduction with ethanol.

The catalytic activity for oxidative coupling of 2,6-di-*t*-butylphenol (**4**) was investigated (Table 1). In the presence of 5 mol % of a catalyst (based on palladium), the reaction was conducted in DMF for 24 h at 80 °C under oxygen. Table 1 summarizes the results. The reaction with the small and well-dispersed Pd nanoparticle gave coupling product **5** quantitatively (entry 1).[14] The use of the larger and aggregated nanoparticle resulted in

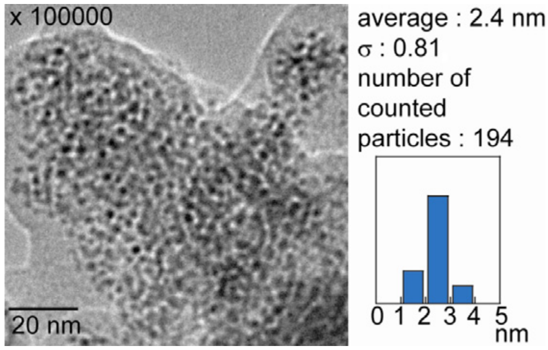
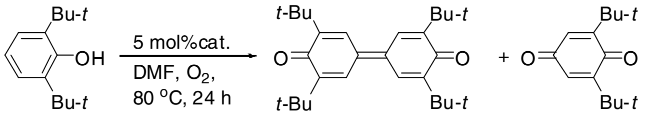


Figure 3. TEM image of **2b** prepared by the reduction of **1** with $NaBH_4$.

Table 1. Oxidative coupling of 2,6-di-*t*-butylphenol



4 **5** **6**

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

[a] Determined by ^{1}H NMR with an internal standard (1,1′,2,2′-tetrabromoethane).

[b] Prepared by the reduction with $NaBH_4$.

[c] Prepared according to Ref. 15.

decrease in the yield of **5** (entry 2). In the absence of Pd nanoparticle, **5** and quinone **6** were obtained in 65% and 12% yield, respectively (entry 3). On the other hand, when the polyvinylpyrrolidone nanoparticle, PVP/Pd[15] was used instead of PANI/Pd nanoparticle, the yield was lower (entry 4).

In summary, the pre-organization of the Pd(II) species on PANI through complexation is effective to synthesize the well-dispersed and small-sized nanoparticle. The present method is considered to be generally applicable to other π-conjugated compound/metals nanoparticles, and even heterometallic nanoparticles. PANI/Pd nanoparticle is expected to serve as an efficient redox catalyst in various oxidative reactions.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.02.059.

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10. *Experimental procedure*: To a stirred solution of polyaniline (142.5 mg) in THF (100 mL) was dropwise added a solution of $Pd(OAc)_2$ (58.4 mg) in THF (100 mL) at room temperature over 30 min under argon. The reaction mixture was stirred at room temperature for 1 h. The appeared precipitation was collected by filtration through a membrane filter, washed with THF, and dried in vacuo to give PANI/Pd(II) complex **1** (174.3 mg, 87%) as a dark blue solid: IR (KBr)/cm^{-1} 3266, 3025, 1589, 1506, 1307, 1156, 821; UV–vis, λ_{max} (2.0×10^{-4} M; THF)/nm 301, 679.
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washed with deionized water, and dried in vacuo to give PANI/Pd nanoparticle **2b** (55.6 mg) as a dark blue solid: IR (KBr)/cm^{-1} 3382, 3025, 1594, 1496, 1289, 1166, 813; UV–vis, λ_{max} (1.0×10^{-4} M; DMSO)/nm 331, 626; elemental analysis $C_{36}H_{30.14}N_{5.55}Pd_1$.

13. The palladium density was determined by elemental analysis.
14. *Experimental procedure*: To a stirred solution of 2,6-di-*t*-butylphenol (**4**) (20.7 mg, 0.10 mmol) in DMF (1 mL) was added PANI/Pd nanoparticle (3.3 mg, 0.005 mmol for Pd) at room temperature under oxygen. After stirring at 80 °C for 24 h, the reaction mixture was filtered through Celite. The filtrate was poured into the mixture of water and ethyl acetate. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The yields of 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (**5**) [2455-14-3] and **6** were determined by ^{1}H NMR with 1,1′,2,2′-tetrabromoethane as an internal standard.
15. PVP/Pd was prepared by the reported procedure: Hirai, H.; Chawanya, H.; Toshima, N. *React. Polym.* **1985**, *3*, 127–141.