# Hybrid of Polyaniline/Iron Oxide Nanoparticles: Facile Preparation and Catalytic Application

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The facile preparative method of iron oxide nanoparticles with polyaniline was developed by thermal reaction of Fe(acac)$_3$. The efficient catalytic activity was demonstrated in the oxidative coupling of 2,6-di-*t*-butylphenol.

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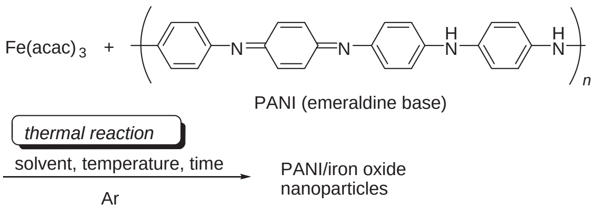
Hybrids of metal oxide nanoparticles and $\pi$-conjugated polymers are expected to create a novel class of electrical device materials and catalysts due to the characteristic properties as electron mediators.[1] Polyaniline (PANI) is one of the most important $\pi$-conjugated compounds as documented well. Some reports described the preparation and characterization of PANI/metal oxide nanohybrids, such as PANI/TiO$_2$[2] and PANI/Iron oxide nanoparticles.[3] On the other hand, we have studied the synthesis of d,$\pi$-conjugated complexes of PANI and its derivatives with various metal salts, such as Pd$^{II}$ and Cu$^{II}$, and even heterometals.[4,5] Furthermore, PANI serves as a redox-active ligand in the transition-metal-catalyzed oxidation reaction.[6] Recently, the synthesis of PANI/Pd nanoparticles based on template method and catalytic application were demonstrated.[7] The synthesis of PANI/iron oxide nanohybrids is considered to permit useful catalysts and electrical materials. However, the catalytic application including carbon–carbon bond formation has not been investigated with PANI/Iron oxide nanoparticles, to our knowledge.

Various methods to prepare iron oxide nanoparticles were reported so far.[8] The size and dispersity of the nanoparticles have been focused on, and recently the size control below 10 nm has been reported. Conventionally, they were prepared from an aqueous solution of FeCl$_2$ and FeCl$_3$ with a surfactant under the basic conditions.[9] Some reports describe the decomposition of Fe(acac)$_3$ in the presence of alcohol, amine, or carboxylic acid having a long alkyl group in an organic solvent.[10] Metal carbonyl was thermally decomposed and oxidized to afford the iron oxide nanoparticles.[11] More recently, thermal reaction of Fe$^{III}$ salts without any additives was found to give the iron oxide nanoparticles when 2-pyrrolidone was used as a solvent.[12] Herein, we report the facile preparation of small-sized and well-dispersed iron oxide nanoparticles with PANI through thermal reaction of Fe(acac)$_3$ and their application to the oxidative coupling of 2,6-di-*t*-butylphenol.

Fe(acac)$_3$ was employed as a single iron source. Thermal reaction was carried out in the presence of PANI (the emeraldine base purchased from Aldrich, $M_W$ = ca. 10000) under argon in various solvents. After stirring for several hours, the reaction mixture was diluted with water to form the precipitate. The suspension was filtered through a membrane filter. The residue was thoroughly washed with deionized water and dried. The obtained solid was observed by TEM. Table 1 summarizes the results. The use of THF and dioxane did not afford the nanoparticles (Entries 1 and 2, respectively). TEM images for the sample prepared in NMP exhibited the obscurely visible particles (Entry 3). The nanoparticles were obtained after stirring in 2-pyrrolidone and DMF for 6 h at ca. 150 °C (Entries 4 and 5, respectively).[15] The TEM image of the particles prepared in DMF (Entry 5) was shown in Figure 1. The particle size was distributed in the range of diameter 3–9 nm (average diameter = 5.6 nm, standard deviation $\sigma = 1.1$, number of counted particles = 212). The particles were relatively dispersed well. EDX experiment showed the presence of Fe. The observed nanoparticles were assigned to iron oxide judging from the reported thermal reaction of Fe(acac)$_3$,[13] although it was difficult to determine the oxidation state, Fe$_3$O$_4$ or Fe$_2$O$_3$. The reaction mechanism might be explained as reported reactions in Refs. 12 and 13. The characteristic absorptions for polyaniline were observed in the IR spectrum (1596 cm$^{-1}$ for the quinonediimine and 1490 cm$^{-1}$ for the phenylenediamine). There were no peaks derived from Fe(acac)$_3$. The UV–vis spectrum showed the charge-transfer (CT) absorption between the benzenoid and quinoid moieties of PANI at around 600 nm. Reaction at a lower temperature (100 °C) did not give the nanoparticles (Entry 6). The TEM images after stirring in DMF for 3 h did not show the sharply visible particles (Entry 7), which suggests the reaction time is too short to grow the particles. On the other hand, the aggregated particles were observed after stirring in DMF for 24 h (Entry 8).

The catalytic activity of the thus-obtained nanoparticles was investigated in the oxidative coupling of 2,6-di-*t*-butylphenol

**Table 1.** Synthesis of PANI/iron oxide nanoparticles



| Entry | Solv. | Temp /°C | Time /h | Diameter /nm | Dispersity |
|---|---|---|---|---|---|
| 1 | THF | 66 | 6 | — | — |
| 2 | Dioxane | 100 | 6 | — | — |
| 3 | NMP | 150 | 6 | Few visible particles | |
| 4 | 2-Pyrrolidone | 150 | 6 | 3–12 | Well[a] |
| 5 | DMF | 153 | 6 | 3–9 | Well[a] |
| 6 | DMF | 100 | 6 | — | — |
| 7 | DMF | 153 | 3 | Few visible particles | |
| 8 | DMF | 153 | 24 | — | Aggregated[b] |

[a] The particles were relatively dispersed well (each particle is almost independent in the TEM image). [b] The particles were aggregated together to form the >50 nm-sized particles.

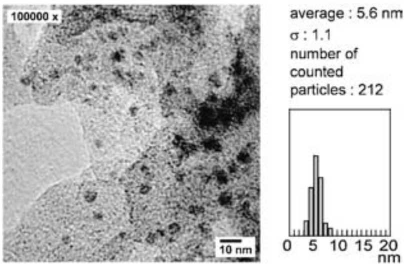
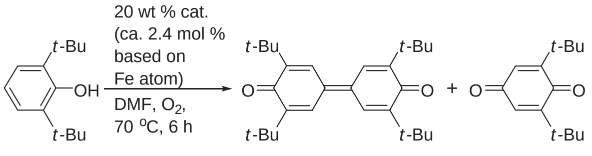


**Figure 1.** The TEM image and size distribution histogram of the PANI/iron oxide nanoparticles prepared under the conditions of Entry 5 in Table 1.

(**1**).[14] In the presence of 20 wt % of the catalyst, the reaction was conducted in DMF for 6 h at 70 °C under oxygen. Table 2 summarizes the results. The reaction with the small and well-dispersed iron oxide nanoparticles prepared under the conditions of Entry 5 in Table 1 gave the coupling product **2** in a good yield (84%, Entry 1).[15] The use of the aggregated nanoparticles (2.4 mol % based on iron atom of $Fe_3O_4$) resulted in significant decrease in the yield of **2** (Entry 2) and a small amount of the quinone **3** was obtained. In the absence of PANI and the iron oxide nanoparticles with PANI, the reaction did not proceed at all (Entries 3 and 8). Only PANI or $Fe(acac)_3$ (2.4 mol %) catalyzed the reaction a little to afford **2** in a low yield (Entries 5 and 6). On the other hand, the presence of both of them resulted in the moderate conversion (Entry 7). When the iron oxide nanoparticles ($Fe_3O_4$) covered with long alkyl chains were used instead of the PANI/iron oxide nanoparticles,[10b] only a trace amount of **2** was obtained (Entry 4). To confirm the effect of oxygen, the reaction was carried out under argon (Entry 9) to result in a low yield, suggesting that oxygen is necessary for this reaction.

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



**1** **2** **3**

| Entry | Catalyst | Yield/%[a] | | |
|---|---|---|---|---|
| | | **1** | **2** | **3** |
| 1 | PANI/iron oxide nanoparticles (Entry 5 in Table 1) | 0 | 84 | 0 |
| 2 | PANI/iron oxide particles (aggregated)[b] | 73 | 4 | 5 |
| 3 | Iron oxide particles (aggregated, ca. >100 nm)[c] | 98 | 0 | 0 |
| 4 | Iron oxide nanoparticles ($Fe_3O_4$) covered with aliphatic chains (3–5 nm)[10b] | 88 | 2 | 0 |
| 5 | PANI | 79 | 8 | 0 |
| 6 | $Fe(acac)_3$ | 63 | 18 | 2 |
| 7 | PANI and $Fe(acac)_3$ | 12 | 70 | 2 |
| 8 | — | 98 | 0 | 0 |
| 9 | PANI/iron oxide nanoparticles (Entry 5 in Table 1)[d] | 87 | 12 | 0 |

[a] $^1H$ NMR yield (1,1,2,2-tetrabromoethane as an internal standard). [b] Prepared by mixing of PANI and the aggregated iron oxide particles employed in Entry 3. [c] The aggregated iron oxide particles were prepared according to the equation $FeCl_2 + 2FeCl_3 + NaOH \rightarrow Fe_3O_4$ particles, and confirmed by TEM. [d] Reaction was carried out under argon.

In conclusion, we developed the facile preparation of the iron oxide nanoparticles with PANI by thermal reaction in DMF. The catalytic activity was demonstrated in the oxidative coupling of 2,6-di-*t*-butylphenol. It should be noted that the PANI/iron oxide nanoparticles were applied to the catalytic oxidation in organic synthesis for the first time. PANI/iron oxide nanoparticles are expected to serve as an efficient redox catalyst in various oxidative reactions.

The authors thank Professors K. Niihara and T. Sekino, and Dr. S. Seino at Osaka University for TEM analysis. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas "Chemistry of Concerto Catalysis" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

This paper is dedicated to the memory of Professor Yoshihiro Matsumura.

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Published on the web (Advance View) December 15, 2007; doi:10.1246/cl.2008.68