

# Core-Satellite Heterostructure of $\text{Fe}_3\text{O}_4$ -Pd Nanocomposite: Selective and Magnetically Recyclable Catalyst for Decarboxylative Coupling Reaction in Aqueous Media

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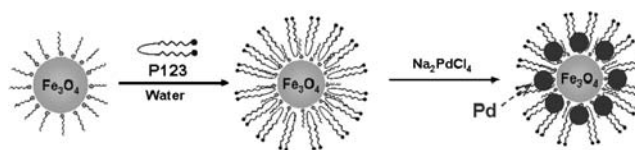
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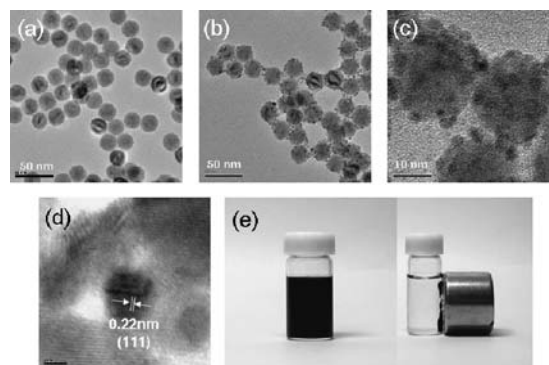
$\text{Fe}_3\text{O}_4$ -Pd nanocomposite having core-satellite heterostructure, prepared through the reaction of Pluronic polymer (P123,  $\text{PEO}_{19}$ - $\text{PPO}_{69}$ - $\text{PEO}_{19}$ )-coated  $\text{Fe}_3\text{O}_4$  nanoparticle and  $\text{Na}_2\text{PdCl}_4$ , showed high catalytic activity, selectivity, and reusability for decarboxylative coupling reactions in aqueous media.

The utilization of nanoparticles for catalysis of organic reactions is of great recent interest.<sup>1</sup> As the size of particle decreases, larger fraction of active metal atoms is exposed at the surface and, consequently, nanoparticles of transition metals often exhibit as high activity as molecular catalysts. Especially, nanoparticles of noble metals such as Pd and Pt have been extensively employed for various reactions, such as olefin hydrogenation and cross-coupling reactions between  $\text{sp}^2$ - $\text{sp}^2$  carbons.<sup>1-3</sup> On the other hand, the small size of nanoparticles makes their separation from reaction solution and recycling difficult, which obstructs their utilization for environment friendly process. In order to circumvent such a recycling problem, the immobilization of nanoparticles on superparamagnetic support matrix, which can be reversibly flocculated and dispersed with applying external magnetic field, has been examined very recently.<sup>4,5</sup> For instance, Ying and co-workers reported nanocomposites containing Pd nanocluster on silica-coated  $\text{Fe}_3\text{O}_4$  particle and their catalysis for hydrogenation reaction.<sup>4c</sup> Although the immobilization can provide nanoparticle catalysts with the recyclability, they still require an organic solvent as a reaction medium. Recently, the organic reaction in aqueous solution has attracted tremendous attention for many catalytic reactions owing to increasing demand for environment friendly processes.<sup>6</sup>

In this respect, we have been making an effort to develop magnetically recyclable nanoparticle catalyst system which enables the organic reactions in aqueous media. Recently, some of us helped develop fabrication of uniform Pd nanoparticles from aqueous solution by using triblock Pluronic copolymer both as a reductant and as a surface capping agent.<sup>7</sup> Based on this, it occurred to us that the surface coating with Pluronic polymer would provide the magnetic nanoparticles with water-dispersity and allow the growth of Pd nanoparticles only at the magnetic nanoparticle surface. It was also envisioned that nanoparticle surface stabilized by Pluronic copolymer would act as nanoreactors to induce the solubilization of organic reactants and allow the reactants to interact more intimately with the Pd nanoparticles, ultimately, catalyzing the reaction in aqueous media. The present communication reports preparation of  $\text{Fe}_3\text{O}_4$ -Pd nanocomposite having core-satellite heterostructure (Scheme 1) and their successful utilization for catalyzing decarboxylative reactions in aqueous media. To the best of our knowledge, this is the first report for the use of Pd nanoparticles for coupling reac-



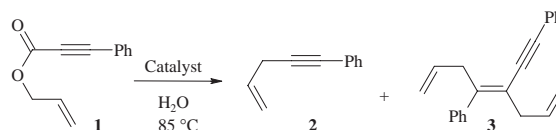
**Scheme 1.** Synthetic approach for Pd- $\text{Fe}_3\text{O}_4$  nanocomposite.



**Figure 1.** TEM images of PCMNP (a) and Pd-MNP (b), (c). (d) HRTEM image focusing a Pd nanoparticle on  $\text{Fe}_3\text{O}_4$  surface. (e) Pictures showing magnetic attraction of Pd-MNP.

tion between  $\text{sp}$  and  $\text{sp}^3$  carbon. The Pd- $\text{Fe}_3\text{O}_4$  nanocomposite showed excellent and selective catalytic performance and was conveniently separated and recycled by simply applying external magnetic field.

The superparamagnetic  $\text{Fe}_3\text{O}_4$  nanoparticles of 20 nm in particle diameter stabilized by oleic acid were prepared through the previously reported procedure.<sup>8</sup> The surface coating of Pluronic copolymer (P123,  $\text{PEO}_{19}$ - $\text{PPO}_{69}$ - $\text{PEO}_{19}$ ) was conducted by mixing  $\text{Fe}_3\text{O}_4$  nanoparticles and P123 in  $\text{CHCl}_3$  solution, evaporating solvent, and annealing at  $150^\circ\text{C}$  in vacuo for 1 h. The addition of water and filtering off floating matters generated transparent dark brown suspension of well-dispersed  $\text{Fe}_3\text{O}_4$  nanoparticles (Pluronic copolymer-Coated Magnetic NanoParticle, PCMNP, Figure 1a). Isolation of PCMNP from excess Pluronic polymer was done by repeating ultracentrifugation and dispersion in water. For the introduction of Pd nanoparticles, an aqueous solution containing  $\text{Na}_2\text{PdCl}_4$  was reacted with a suspension of PCMNP and vigorously shaken at room temperature. Within 2 h, a dark brown precipitate appeared, indicating the formation of Pd nanoparticles on the surface of PCMNP. The precipitate was concentrated, isolated by magnetic decantation and washed with water three times. The resulting solid are well dispersed in water by shaking, vortexing, or sonication, resulting in clear dark-brown-colored dispersion, and they can be easily attracted within several minutes by placing a small magnet on a side of

**Table 1.** Catalytic decarboxylic coupling reaction of allyl alkynoate


Entry	Catalyst	$T/^{\circ}\text{C}$	$t/\text{h}$	Yield/% <sup>a</sup>
1	5 mol % Pd/Fe <sub>3</sub> O <sub>4</sub>	85	2	25(3)(70) <sup>b</sup>
2	5 mol % Pd/Fe <sub>3</sub> O <sub>4</sub>	85	12	95(3)
3	Recovered from Entry 2	85	12	88(3)
4	5 mol % Pd/C	85	12	20(4(2):1(3)) <sup>c</sup>
5	5 mol % Pd(PPh <sub>3</sub> ) <sub>4</sub>	85	6	92(4(2):1(3)) <sup>c</sup>

<sup>a</sup>Isolated yield. <sup>b</sup>Yield in parenthesis is of the recovered reactant. <sup>c</sup>The ratio was determined by <sup>1</sup>H NMR.

vessel (Figure 1e). Most of solids were aggregated and precipitated within 2 h after standing at room temperature and could be easily re-dispersed by shaking, vortexing, or sonication.

Transmission electron microscopy (TEM) reveals the generation of Pd nanoparticles having  $2.1 \pm 0.4$  nm in average size around Fe<sub>3</sub>O<sub>4</sub> nanoparticle and core-satellites heterostructure (Figures 1b and 1c). The lattice distance, 2.40 Å, measured from the satellite nanoparticle is well consistent with known parameters of a face-centered cubic (fcc) Pd crystal structure, confirming the formation of highly crystalline Pd nanoparticles (Figure 1d). There were not observed any discernable changes in the shape, size, and size distribution of Fe<sub>3</sub>O<sub>4</sub> nanocrystals during the reaction. The formation of core-satellites structure can be understood by the reduction of Pd<sup>II</sup> by P123 copolymer and the occurrence of seeding and growth of Pd nanoparticles confined at the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticle, in accordance with our anticipation.<sup>9</sup>

Pd nanoparticles supported on magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticle (Pd-MNP) were then examined for catalysis of decarboxylic coupling reaction of allyl alkynoate, which was developed with Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst by Rayabarapu and Tunge, in aqueous solution.<sup>10</sup> The reaction was carried out by the addition of a sparingly water-soluble substrate into an aqueous suspension of Pd-MNP. As presented in Table 1, Pd-MNP showed good catalytic activity for 3-phenyl-2-propynoic acid 2-propenyl ester, **1**, providing 95% yield of decarboxylated product through the reaction at 85 °C for 12 h. Under the same reaction condition, commercially available Pd on charcoal afforded 20% yield. The most noteworthy is the excellent selectivity of the reaction catalyzed by Pd-MNP. While the treatment of **1** with Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd on charcoal gave a mixture of an allylphenylacetylene, **2**, and its dimerized product, **3**, the use of Pd-MNP afforded **3**, exclusively. In order to check the possibility of conversion between **2** and **3** during the reaction, isolated **2** was treated with Pd-MNP in the presence of **1**,<sup>11</sup> and the complete conversion of **1**, the formation of dimerized product **3**, and still remaining of **2** were observed from the reaction, confirming the catalytic selectivity of Pd-MNP. The origin of the catalytic selectivity between **2** and **3** is unclear in this stage but may be due to the easier coupling between Pd intermediate complexes formed close to each other on nanoparticle surface. In order to investigate its recyclability, Pd-MNP was isolated by a small magnet paced at the bottom of the reaction vessel and reused for consecutive reaction. The ac-

tivity of the second reused catalyst was only slightly reduced, and ICP measurement showed 85% of Pd species was remaining.<sup>12</sup>

In conclusion, we prepared Pd-Fe<sub>3</sub>O<sub>4</sub> nanocomposite having core-satellite heterostructure by generating of Pd nanoparticles at the Pluronic polymer-coated surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticle. We demonstrated the high activity and selectivity of the Pd-Fe<sub>3</sub>O<sub>4</sub> nanocomposite for catalyzing decarboxylative coupling reaction in aqueous media, avoiding hazardous organic solvent and its recovery and reusability upon application of magnetic separation.

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