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Rose-like Pd-Fe$_3$O$_4$ hybrid nanocomposite-supported Au nanocatalysts for tandem synthesis of 2-phenylindoles

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Abstract
A facile synthesis of rose-like Pd-Fe$_3$O$_4$ nanocomposites via controlled thermal decomposition of Fe(CO)$_5$ and reduction of Pd(OAc)$_2$, followed by the immobilization of Au nanoparticles (NPs) onto the Pd-Fe$_3$O$_4$ supports, has been reported. The morphology of these hybrid nanostructures could be easily controlled by varying the amount of Fe(CO)$_5$ and the reaction temperature. Moreover, the synthesized Au/Pd-Fe$_3$O$_4$ catalyst exhibited high catalytic activity for the tandem synthesis of 2-phenylindoles and demonstrated magnetic recyclability.

Key words
Hybrid; Nanoparticles; Heterogeneous; Catalyst; Tandem reaction

In recent years, numerous attempts have been made toward the design and synthesis of hybrid nanostructures with defined multicomponents by controlling the size and shape through solution-growth fabrication.$^{1-3}$ Many studies have reported the incorporation of two or more distinct nano materials into one unit with increased functionality.$^{4,6}$ The presence of multicomponent functions, combined with the enhanced chemical and physical properties, make hybrid nanostructures suitable for promising new applications.

Among the bimetallic hybrid nanostructures, Han and coworkers$^7$ reported the one-step aqueous synthesis of bimetallic core-shell Au-Pd nanoparticles (NPs) with a well-defined octahedral shape. Sun et al.$^8$ conducted structure-dependent FePt NP catalysis and demonstrated that the intermetallic FePt NP is a considerably better catalyst for oxygen reduction reactions (ORR). Furthermore, various multimetallic NPs have been reported by the Ying$^9$ and Sun$^{10}$ groups. Ying and coworkers$^9$ reported a simple chemical synthetic route for producing FePt-Au hybrid nanostructures as catalysts for ORR reactions. Sun et al.$^{10}$ presented a unique approach for synthesizing core/shell-structured Pd/FePt NPs. Recently, the Sun group reported the one-pot synthesis of urchin-like FePd-Fe$_3$O$_4$ via controlled thermal...
decomposition of Fe(CO)$_5$ and reduction of Pd(acac)$_2$. However, to date, there has been rarely any report on the flower-like structures of Pd-Fe$_3$O$_4$, in spite of the fact that Pd and Fe$_3$O$_4$ are advantageous. Our ongoing interest in the hybrid metal-metal oxide composites, combined with various noble metal NPs, motivated us to investigate Pd-Fe$_3$O$_4$ nanocomposite-supported Au NPs by a facile approach.

With the development of chemical sciences, new protocols bringing greater efficiency and simplicity to organic reactions are highly desirable. Among these protocols, the catalytic synthesis of indole ring systems through cross-coupling/cycloadditions of 2-haloanilines with alkynes has proven to be the most powerful tool, because indole nuclei, which have unique biological activities, are important as building blocks in natural and pharmacological products. However, tandem synthesis of 2-arylindoles from 2-haloanilines, catalyzed by hybrid bimetallic nanocatalysts, is extremely rare in literature. In this work, we report a facile synthesis of rose-like Pd-Fe$_3$O$_4$ nanocomposites, followed by the immobilization of Au NPs onto these Pd-Fe$_3$O$_4$ supports (Scheme 1). These hybrid Au/Pd-Fe$_3$O$_4$ nanostructures showed high catalytic activity for the tandem synthesis of 2-phenylindoles, and demonstrated magnetic recyclability. These nanocomposites showed the excellent point of the hybrid nanocomposites.

![Scheme 1](attachment:image.png) Synthetic scheme of Au/Pd-Fe$_3$O$_4$ nanocomposites

The rose-like Pd-Fe$_3$O$_4$ nanocomposites were synthesized by facile decomposition of Fe(CO)$_5$ and reduction of Pd(OAc)$_2$ in oleylamine (OAm) and 1-octadecene (ODE) (see the Supporting Information). In the synthesis, 0.114 g of Pd(OAc)$_2$, 10 mL of OAm, and 10 mL of ODE were initially mixed at room temperature, and then heated to 120 °C. Under a blanket of argon gas, a controlled amount of Fe(CO)$_5$ was added. Then, the solution was heated to 160 °C at a heating rate of 4 °C/min and maintained at 160 °C for 30 min, before being cooled to room temperature. The product was separated, purified, and redispersed in hexane. Then, the Pd-Fe$_3$O$_4$ solution was injected into Au precursor-OAm solution at 80 °C and stirred for 30 min. The temperature was reduced to room temperature. The sample was centrifuged in ethanol to obtain black precipitates. The products were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Under the described synthetic conditions, the as-synthesized individual hybrid nanosheets, containing Pd and Fe$_3$O$_4$, formed three-dimensional rose-like Pd-Fe$_3$O$_4$ nanocomposites. The Fe/Pd ratios of the composites synthesized at 160 °C were controlled to 64:36-80:20 by increasing the amount of Fe(CO)$_5$ from 0.15 to 0.45 mL.
Fig. 1 shows the scanning electron microscopy (SEM) images of the rose-like Pd-Fe$_3$O$_4$ and Au/Pd-Fe$_3$O$_4$ hybrid nanocomposites with the well-distributed average diameter of 213 nm (Pd-Fe$_3$O$_4$). Au NPs were uniformly immobilized onto the Pd-Fe$_3$O$_4$ supports (Fig. 1b, d). The transmission electron microscopy (TEM) images show Pd-Fe$_3$O$_4$ nanocomposites with an overall Fe/Pd ratio of 64:36 (Fig. 2a, b). The Au NPs immobilized onto Pd-Fe$_3$O$_4$ nanocomposites are shown in Fig. 2c, d. The immobilized Au NPs, with an average diameter of 5.8 nm, are spherical and highly monodisperse (Fig. 2d). The high-resolution TEM (HR-TEM) image of a representative Pd-Fe$_3$O$_4$ nanocomposite (Fig. 2e) shows that the Pd and Fe$_3$O$_4$ structures have well-defined and uniformly spaced lattice fringes with the fringe distance measured to be 0.22 nm of Pd (111) plane and 0.30 nm of Fe$_3$O$_4$ (220) plane, corresponding to the face centered cubic (fcc) Pd and Fe$_3$O$_4$ structures, respectively. Au NPs also have uniformly spaced lattice fringes, with the fringe distance measured to be 0.24 nm, corresponding to the (111) interplanar spacing in the fcc Au structure (Fig. 2f).

![Fig. 1 SEM images of rose-like Pd-Fe$_3$O$_4$ (a,b) and Au/Pd-Fe$_3$O$_4$ (c,d) nanocomposites. The bars in the inset represent (c,d) 200 nm.](image)

The 3D flower-like structures are highly advantageous for sensors, lithium ion batteries, and photocatalysis because of their large specific surface area. To confirm this, we measured the Brunauer-Emmett-Teller (BET) surface area of the Pd-Fe$_3$O$_4$ nanocomposites to be 23.79 m$^2$g$^{-1}$, which is much higher than that of the previously reported hollow and solid sphere-like Fe$_3$O$_4$ microspheres (12.27 and 5.43 m$^2$g$^{-1}$, respectively) because of the individual Pd-Fe$_3$O$_4$ nanosheets. The amount of Fe(CO)$_5$ used during the synthesis process controlled not only the Fe/Pd ratio but also the morphology of the Pd-Fe$_3$O$_4$ nanocomposites. When the amount of Fe(CO)$_5$ was increased from 0.15 mL to 0.30 and 0.45 mL, Pd-Fe$_3$O$_4$ composites still formed, but their diameter decreased constantly, as shown in Fig. S1. Fig. S2 shows the TEM images of three Pd-Fe$_3$O$_4$ nanocomposites synthesized at different temperatures (120, 140,
and 160 °C) for comparison. The thermal decomposition of Fe(CO)$_5$ and reduction of Pd(OAc)$_2$ could not be sufficiently carried out at the decreased temperatures (120 and 140 °C), resulting in the short diameter and aggregations of the Pd-Fe$_3$O$_4$ nanocomposites.

![Fig. 2 TEM images of Pd-Fe$_3$O$_4$ (a,b) and Au/Pd-Fe$_3$O$_4$ (c,d). Au size distribution graph (d). HR-TEM images of Pd-Fe$_3$O$_4$ (e) and Au/Pd-Fe$_3$O$_4$ (f). The bars in the inset represent (a,c) 20 nm.](image)

The structures of Au/Pd-Fe$_3$O$_4$ and Pd-Fe$_3$O$_4$ composites were further characterized by X-ray diffraction (XRD). Fig. 3a shows the XRD patterns of the as-synthesized composites with overall element ratios of 7:77:16 (Au:Fe:Pd) and 64:36 (Fe:Pd). In the case of the Pd-Fe$_3$O$_4$ structure, all the peaks of the XRD pattern could be assigned to the (111), (200), and (220) lattice planes of an fcc Pd crystal structure (JPCDS No. 46-1043) and to the (220), (311), (422), (511), and (440) lattice planes of the cubic spinel structured Fe$_3$O$_4$ (JCPDS No. 19-0629). In the case of Au/Pd-Fe$_3$O$_4$, the immobilized Au NPs are assigned to the (111), (200), (220), and (311) reflections of an fcc Au crystal structure (JCPDS No. 04-0784). Specifically, the broadened diffraction peaks from Au NPs reveal the small size of the crystal domains. Selected area electron diffraction (SAED) pattern was obtained to confirm the crystal structure of Au, Pd and Fe$_3$O$_4$ particles (Fig. S3). The high-angle annular dark-field scanning TEM (HAADF-STEM) image and elemental mapping also reveal that Au, Pd and Fe$_3$O$_4$ are dispersed in the entire area of the composite, confirming the hybrid Au/Pd-Fe$_3$O$_4$ structure (Fig. 3b). The superconducting quantum interference device (SQUID) data showed the
magnetic curves as a function of the applied field at 300 K (Fig. S4). The saturation magnetization value of the Au/Pd-Fe3O4 nanocomposites was 5.49 emu·g⁻¹, which was similar to that of Pd-Fe3O4 (5.67 emu·g⁻¹). Moreover, both the remanence (Mr) and coercivity (Hc) of nanocomposites were close to zero, indicating superparamagnetism. Elemental analysis of Au/Pd-Fe3O4 was confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. S5a). The binding energies of the doublet for Au 4f⁷/₂ (83.2 eV) and Au 4f⁵/₂ (86.8 eV), shown in Fig. S5b, are characteristic of Au⁰. In the case of Pd, the most intensive peak is observed at binding energy around 335.1 eV (3d⁵/₂) and 340.3 eV (3d₃/₂), respectively, indicating their metallic Pd characteristics (Fig. S5c). Fig. S5d shows the XPS signals of the Fe 2p regions, which indicate that both Fe²⁺ and Fe³⁺ show the formation of Fe3O4. An additional satellite peak (719 eV) appears between the Fe 2p₁/₂ (724.8 eV) and Fe 2p₃/₂ (710.9 eV) components and is a characteristic peak of Fe³⁺ in γ-Fe₂O₃, suggesting that the Fe3O4 nanoparticles were partly oxides.¹⁷ The peak shape of C 1s does not exhibit any possible deformation associated with charging effect, showing that Au/Pd-Fe3O4 nanocomposites do not have any noticeable charging effect which might cause the peak position shift and peak shape deformation (Fig. S6). The elemental compositions of the Au/Pd-Fe3O4 nanocomposites were also obtained using energy-dispersive X-ray spectroscopy (Fig. S7).

![Fig. 3 XRD patterns of Pd-Fe₃O₄ and Au/Pd-Fe₃O₄ (a). HAADF-STEM image and elemental mapping of Au/Pd-Fe₃O₄ (b). The bars in each element image represent 50 nm.](image)

To evaluate catalytic activity of Au/Pd-Fe3O4 catalyst, the tandem synthesis of 2-phenylindoles from 2-iodoanilines with phenylacetylenes were performed as a model reaction under different conditions (Table 1). First, the effects of the solvents were examined in the presence of the 0.5 mol% Pd-Fe3O4 catalyst at 120 °C for 18 h (entries 1-3). The use of more polar solvents (DMSO) led to an increase in the conversion because of the superior solubility
of reactant and catalyst in the reaction medium. The influence of bases such as piperidine, LiOAc and CsOAc was studied for the standard reaction (entries 3-5).

Table 1 Tandem synthesis of 2-phenylindoles.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temp. (℃)</th>
<th>Time (h)</th>
<th>Base</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd-Fe₃O₄</td>
<td>120</td>
<td>18</td>
<td>Piperidine</td>
<td>trace&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Pd-Fe₃O₄</td>
<td>120</td>
<td>18</td>
<td>Piperidine</td>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>Pd-Fe₃O₄</td>
<td>120</td>
<td>18</td>
<td>Piperidine</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>Pd-Fe₃O₄</td>
<td>120</td>
<td>18</td>
<td>LiOAc</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>Pd-Fe₃O₄</td>
<td>120</td>
<td>18</td>
<td>CsOAc</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>Au/Pd-Fe₃O₄</td>
<td>120</td>
<td>18</td>
<td>CsOAc</td>
<td>57</td>
</tr>
<tr>
<td>7</td>
<td>Au/Pd-Fe₃O₄</td>
<td>150</td>
<td>18</td>
<td>CsOAc</td>
<td>97</td>
</tr>
<tr>
<td>8</td>
<td>Au/Pd-Fe₃O₄</td>
<td>150</td>
<td>9</td>
<td>CsOAc</td>
<td>97</td>
</tr>
<tr>
<td>9</td>
<td>Au/Pd-Fe₃O₄</td>
<td>150</td>
<td>6</td>
<td>CsOAc</td>
<td>38&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Reaction condition: Au/Pd-Fe₃O₄ catalyst [Au base: 0.18 mol%, Pd base: 0.5 mol%], 2-iodoaniline (0.5 mmol), phenylacetylene (0.6 mmol), base (1.0 mmol), DMSO (2.5 ml). * Determined by using GC-MS spectroscopy based on 2-iodoaniline. †<sup>b</sup> DMF and DMA was used as solvent, respectively. †<sup>d</sup> 0.09 mol% (Au base) of catalyst was used.

The use of CsOAc led to good conversion (48%) compared to piperidine and LiOAc. It was assumed according to the hard-soft acid and base theory that the Cs<sup>+</sup> is the best pearson acid to remove the iodide from the transient palladium NPs by maximization of the soft-soft interaction. Until now, dual-catalytic cross-coupling reactions with gold and palladium have been paid much attention because of novel reactivity unavailable to single-metal systems. These dual-catalytic systems possess higher catalytic activities than single catalytic systems due to electron transfer across the interface and avoid the stoichiometric transmetalation byproducts common to cross-coupling reactions. So, Au/Pd-Fe₃O₄ catalyst showed better catalytic activity than Pd-Fe₃O₄ since the Au NPs used are much efficient in activating phenylacetylene (entries 5 and 6). As expected, 97% conversion was achieved at high temperature (150 °C) (entries 6 and 7). We also tested the effects of the amount of the catalyst and reaction time. Conversion was decreased (59 and 38 %) when short reaction time (6 h) and less amount of catalyst (Au base: 0.09 mol%) were used (entries 8-10). The optimum
reaction conditions were found to be as follows: Au/Pd-Fe₃O₄ (Au base: 0.18 mol%, Pd base: 0.5 mol%); solvent: DMSO (2.5 mL), temperature: 150 °C, reaction time: 9 h (entry 8). Without any additives and ligands, the Au/Pd-Fe₃O₄ catalyst exhibited superior catalytic activity relative to previously reported copper, gold complexes and Au NPs in terms of the turnover frequency (TOF) value.\textsuperscript{22-24} We also tried to compare catalytic activity with previous reported heterogeneous catalysts of our group (Fig. 4).\textsuperscript{25-29} Among them, Au/Pd-Fe₃O₄ showed the highest TOF value at the same condition and this can be contributed to dual-catalytic system between catalytic effective Pd-Fe₃O₄ support and Au NPs. Pd-Fe₃O₄ support could also exhibit high catalytic activity since individual Pd-Fe₃O₄ nanosheets which have high surface area gave Pd\textsuperscript{0} sites acting as catalytically active sites. The Au/Pd-Fe₃O₄ catalyst after the tandem reaction could be totally separated by an external magnet owing to the superparamagnetic property of Fe₃O₄ particles.\textsuperscript{30} The Au/Pd-Fe₃O₄ catalyst was recycled three times and its initial high activity (> 99%) was still maintained without any loss during the recycling process. For the Pd and Au leaching test, the filtrated solution after the catalytic reaction was checked by ICP-AES analysis, resulting in the small Pd and Au content in the solution measured to be 79.8 and 80.9 ppm, respectively. To confirm the effect of leaching in catalytic activity, coupling reaction was conducted in the presence of poly(4-vinylpyridine), which behaves as a poison to trap homogeneous Pd species through chelation in the solution phase, resulting in no obvious change in catalytic activity. Also, we conducted stability test of catalyst through ultrasonic treatment.\textsuperscript{31} First, Au/Pd-Fe₃O₄ catalyst was placed in an ultrasound cleaner for 2.0 h in aqueous solution (0.5 mg/mL). After removing the catalyst, the mass of Au, Pd and Fe atoms escaped from the Au/Pd-Fe₃O₄ was tested. ICP-AES measurements showed that the loss of Au, Pd and Fe atoms in Au/Pd-Fe₃O₄ was under the detection line of the instrument, showing high stability of catalyst (Au: 0.187 ppm, Pd: 0.441 ppm and Fe: 0.448 ppm). We can conclude that the Au/Pd-Fe₃O₄ catalyst maintained catalytic activity and stability, even though particles were slightly leached during the reaction.

![Comparison of catalytic activity with previous reported heterogeneous catalysts in our group.](image.png)

**Fig. 4** Comparison of catalytic activity with previous reported heterogeneous catalysts in our group.
condition: 2-iodoaniline (0.5 mmol), phenylacetylene (0.6 mmol), CsOAc (1.0 mmol), DMSO (2.5 ml), Catalyst (0.36 mol%), 150 °C, 4.5 h.

In conclusion, we have developed a facile synthesis of rose-like Pd-Fe$_3$O$_4$ nanocomposites through controlled thermal decomposition of Fe(CO)$_5$ and reduction of Pd(OAc)$_2$ followed by immobilization of Au NPs onto Pd-Fe$_3$O$_4$ support. These nanocomposites showed higher BET surface area due to rose-like Pd-Fe$_3$O$_4$ nanostructures, resulting in catalytic active Pd-Fe$_3$O$_4$ support. Synthesized dual-catalytic Au/Pd-Fe$_3$O$_4$ catalyst exhibited better catalytic activity and recyclability than previous reported many catalysts for the tandem synthesis of 2-phenylindoles. It has been demonstrated that the NPs immobilized on hybrid nanocomposite have great potential to be tailored with respect to the activity, selectivity, and stability of their numerous combinations.

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