

# The synthesis and applications of a micro-pine-structured nanocatalyst†

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Dendritic nanoferrites with a micro-pine morphology have been synthesized for the first time under microwave irradiation conditions without using any reducing or capping reagent; the nanoferrites were then functionalized and coated with Pd metal, which catalyzes various organic transformations.

The self-assembly of nanoparticles, such as nanoclusters, nanowires, nanobelts and nanotubes,<sup>1–3</sup> is a *modus operandi* for designing novel sensors, circuits and devices at the nano- and microscale.<sup>4–7</sup> Fractal structures are common in nature across all areas, from self-assembled molecules, to the shapes of coastlines, to the distribution of galaxies, and even to the shapes of clouds.<sup>8</sup> Dendritic hyperbranched structures are formed by hierarchical self-assembly in a non-equilibrium environment; techniques for assembling nanoparticles into superstructures include the use of shear stress, solvent evaporation, lithography, templates, and optical, electrical and magnetic fields.<sup>9–15</sup> The study of self-assembled fractal patterns in chemical synthesis has revealed that the size, shape and chemical functionality of such structures make them potential candidates for the design and invention of new functional nanomaterials.<sup>1–7</sup> In recent years, extensive research has been performed on nanomaterials of various dimensions, such as magnetic metals and metal oxides, which has led to substantial advances in nanomaterial synthesis.<sup>16,17</sup> However, it is exigent to develop easy and sustainable approaches for building hierarchically self-assembled fractal architectures of an assortment of materials.

Microwave (MW) chemistry has been widely used in synthetic organic chemistry, with enhanced reaction rates, selectivity and product yields.<sup>18</sup> This technique is also useful for the synthesis of high quality nanomaterials *via* direct MW heating of their molecular precursors.<sup>19–22</sup> However, to the best of our knowledge, the hierarchical self-assembly of nanomaterials under MW irradiation has not been reported. Engaged in the development of greener and more sustainable pathways for organic transformations<sup>18</sup> and nanomaterials,<sup>23</sup> herein we report an easy and rapid synthesis of single-crystal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with a dendritic micro-pine nanostructure (Fig. 1) and its catalytic application in various organic transformations under MW irradiation conditions.

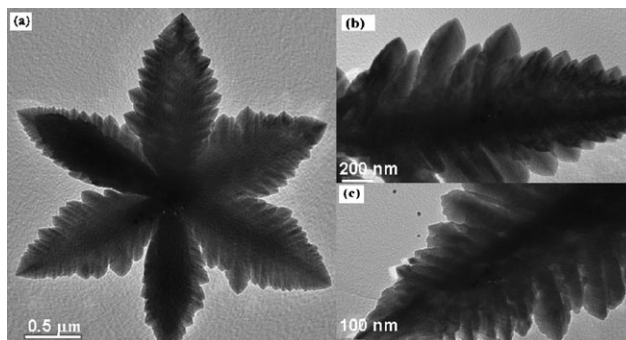


Fig. 1 TEM image of dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

This material was synthesized using a hydrothermal technique by simply heating K<sub>4</sub>[Fe(CN)<sub>6</sub>] in water at 150 °C under MW irradiation conditions for 3 h, with a moderate yield (40%). During the reaction, the [Fe(CN)<sub>6</sub>]<sup>4–</sup> ion, which has six equivalent cyanide ions, dissociated in water and grew rapidly along its six crystallographic directions, yielding the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. The morphology of these particles appeared to be like a pine tree (Fig. 1), hence the term micro-pine particle. Because of this unique morphology, these materials will have significant applications in biomedical science and catalysis. TEM images of the synthesized micro-pine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles show a single-crystal structure. A closer inspection of these particles revealed well-defined and highly ordered branches (Fig. 1(b) and (c)) distributed on both the sides. The TEM observations also revealed that the micro-pine dendrites self-assemble to form a six-fold symmetric structure (Fig. 1(a)).

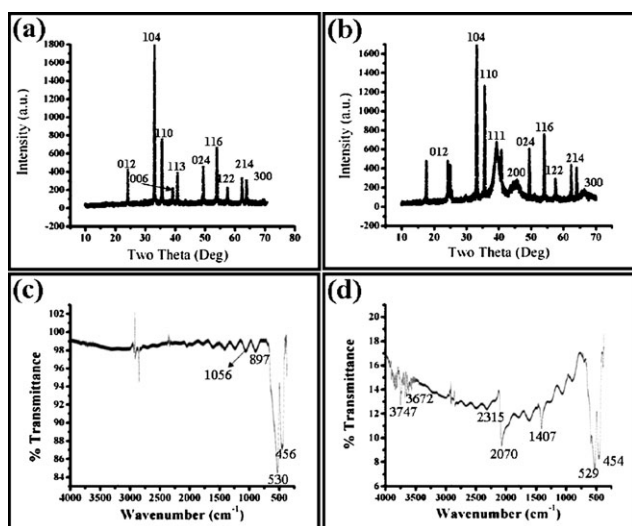
Further structural characterization of this material was carried out by powder XRD (Fig. 2(a)) and FT-IR (Fig. 2(c)), which show that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase has a rhombohedral structure (JCPDS 01-089-0596), with lattice parameters of  $a = 0.50205$  and  $c = 1.3457$  nm.

The effect of substrate concentration and reaction temperature on the morphology of the nanoparticles was also studied. It was observed that with an increase in the concentration, the sharpness of branched dendrite particles decreased and material with slightly branched particles was formed (see the ESI† for TEM images at various concentrations). The reaction temperature plays a crucial role in this synthesis. At 150 °C, moderate to good product yields were obtained in 3 h; however, below this temperature, the formation of nanoparticles required extended reaction times.

To investigate the utility of this new and highly structured material, it was tested as a catalyst for organic transformations involving various C–C coupling and hydrogenation reactions, as these are significant processes in organic chemistry. The first

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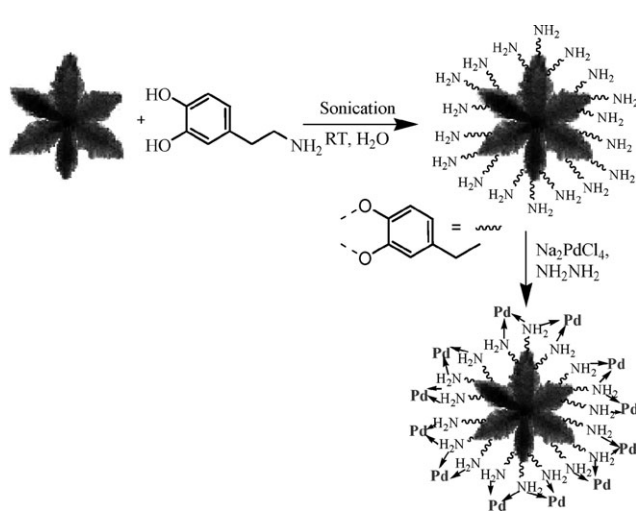
† Electronic supplementary information (ESI) available: Experimental procedures and spectral data of single-crystal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, details of various organic transformations, and catalyst recycling and leaching tests. See DOI: 10.1039/b814715a



**Fig. 2** The XRD (a and b) and FT-IR (c and d) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and functionalized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, respectively.

step in the accomplishment of this goal was the functionalization of the pine tips of synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by an organic functional group, which could then act as a ligand in metal-catalyzed reactions (Scheme 1). The catalyst was prepared by sonicating the nanoparticles with dopamine in water for 2 h, followed by the addition of a Pd salt at basic pH. Material with Pd nanoparticles on the tips of amine-functionalized micro-pine ferrites was obtained in excellent yield. FT-IR and XRD evidently confirmed the anchoring of dopamine and Pd particles onto the ferrite surfaces (Fig. 2(b) and (d)). The IR band at 2070 cm<sup>-1</sup> is characteristic of linear CO species adsorbed onto Pd and the band at 1407 cm<sup>-1</sup> is due to the C–N stretching vibration of the dopamine; XRD peaks occurred at  $2\theta = 15^\circ$  ( $d = 5.05 \text{ \AA}$ ) and  $25^\circ$  ( $d = 3.56 \text{ \AA}$ ) for the N–Pd complex. The weight percentage of Pd was found to be 7.26% by ICP-AES analysis.

The formation of C–C bonds *via* Pd-catalyzed cross-coupling reactions plays a crucial role in synthetic organic chemistry. Particular attention has been paid to the coupling reaction of aryl halides with boronic acids, alkenes and

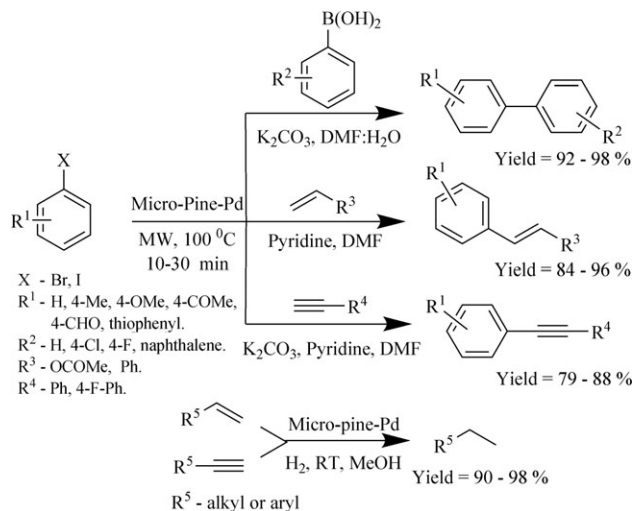


**Scheme 1** The synthesis of functionalized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with a Pd coating.

alkynes, commonly called Suzuki, Heck and Sonogashira reactions, respectively.<sup>24</sup> The practical use of the ever increasing number of tailor-made transition metal catalytic species is connected with the problem of separation and reuse of the rather costly catalyst systems. To overcome these problems, we have explored this Pd-containing material as a heterogeneous catalyst for these coupling and hydrogenation reactions (Scheme 2).

Micro-pine Pd displayed a high catalytic activity in Suzuki reactions (ESI, Table 1†). Aryl halides with various functional groups efficiently reacted with boronic acids to yield the coupling products in good to excellent yields. 2-Iodothiophene underwent a smooth reaction with various boronic acids, providing a useful pathway for the synthesis of aryl-substituted thiophene heterocycles. The coupling of aryl halides with alkenes (Heck reaction) occurred to yield the corresponding products in good yields. A variety of substituted aryl bromides and iodides reacted readily (ESI, Table 2†) and the rates were barely influenced by the electronic effects of the substituents on the aromatic ring of the halides, showing the high activity of the catalyst. The utility of this nanocatalyst was then explored in the Sonogashira reaction using a variety of substrates (ESI, Table 3†), and excellent coupling products were obtained within 45 min. The use of MW-assisted chemistry was due to the efficiency of the interaction of the polar nanocatalysts with the MWs; the reaction mixture could be rapidly heated under MW irradiation.<sup>18a,b</sup>

Metal-catalyzed hydrogenations of alkynes and alkenes, which are generally catalyzed by homogeneous catalysts, have received much interest in the past because of the immense number of opportunities that exist to prepare high-value products. Thus, there is an urgent need to develop less expensive and easily available heterogeneous metal catalysts. In view of this fact, we undertook the hydrogenation reactions using the micro-pine Pd catalyst (ESI, Table 4†). The hydrogenation of a range of unsaturated compounds was explored, and the reactions proceeded smoothly at room temperature to afford the desired products. Alkynes and alkenes were hydrogenated to yield the corresponding alkanes in excellent yields. Heterocyclic alkynes were also reduced in short reaction times



**Scheme 2** Micro-pine Pd-catalyzed reactions.

and this aspect of the protocol bodes well for the application of this catalyst to the total synthesis of drug molecules. This method can also be adopted for the reduction of nitro groups to their corresponding amines, indicating the versatility of this catalyst system.

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are very important factors. To clarify this issue, we established a set of experiments for the Suzuki reaction of iodobenzene and phenylboronic acid using the micro-pine Pd catalyst. After completion of the first reaction to afford the corresponding product, the catalyst was recovered, washed with methanol and finally dried at 50 °C. A new reaction was then performed with fresh iodobenzene and phenylboronic acid under the same conditions. The catalyst could be used at least five times without any change in its activity. Similar experiments were also conducted for the Heck (substrates: iodobenzene and methyl acrylate), Sonogashira (substrates: iodobenzene and phenyl acetylene) and hydrogenation (substrate: phenyl acetylene) reactions. The nanocatalyst showed excellent recyclability in all of the reactions and no catalyst deterioration was observed, confirming its high stability (see the ESI†).

The heterogeneity and metal leaching of this catalyst in the Heck reaction of iodobenzene and methyl acrylate were examined by the modified 'hot filtration' test. The reaction was stopped at 25% conversion (10 min reaction time), and after 1 min, the reaction mixture turned to a clear liquid as the solid catalyst was deposited on the magnetic bar. Half of the liquid reaction mixture was transferred to another reaction tube. After an additional 20 min MW exposure at 100 °C, the portion containing the nanocatalyst showed 95% conversion, while the catalyst-free portion showed 30% conversion, evidently proving the heterogeneity of catalyst. Metal leaching was then studied by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of the catalyst before and after the reaction. The Pd concentration of the catalyst was found to be 7.26% before the reaction and 7.12% after the reaction, and there was no Pd detected in the final product, confirming negligible Pd leaching. This is due to well-defined amine binding sites located on the surfaces of the micro-pine ferrites (Scheme 1), which act as pseudo-ligands by non-covalent binding with the Pd through metal–ligand interactions. The anchoring minimizes deterioration and metal leaching, and allows efficient catalyst recycling. The most important criterion in choosing a catalyst is the ease of metal recovery. It would be preferable to use a micro-pine Pd catalyst, provided that the reaction produces excellent yields and that the catalyst leaves no remnants of metal in the end product, since metal contamination is highly regulated by the pharmaceutical industry. All of the above conditions were satisfied by this recyclable micro-pine Pd catalyst.

Thus, we have developed a convenient synthesis of dendritic nanoferrites with a micro-pine structure under MW irradiation

conditions. Materials were readily prepared from inexpensive starting materials in water without using any reducing or capping reagent. This synthetic concept could ultimately enable the fine tuning of material responses to magnetic, electrical, optical and mechanical stimuli. The nanoferrites were then functionalized and coated with Pd metal, which catalyzes various C–C coupling and hydrogenation reactions with high yields. Also, the ease of recovery and high efficiency, combined with the intrinsic stability of this material, make this method robust and economic.

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