

Magnetically Recoverable Pd/Fe₃O₄ Core-Shell Nanowire Clusters with Increased Hydrogenation Activity.

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Core-shell nanostructures are promising candidates for the next generation of catalysts due to synergistic effects which can arise from having two active species in close contact, leading to increased activity. Likewise, catalysts displaying added functionality, such as a magnetic response, can increase their scientific and industrial potential. Here, we synthesize Pd/Fe₃O₄ core-shell nanowire clusters and apply them as hydrogenation catalysts for an industrially important hydrogenation reaction; the conversion of acetophenone to 1-phenylethanol. During synthesis, the palladium nanowires self-assemble into clusters which act as a high surface area framework for the growth of a magnetic iron oxide shell. We demonstrate excellent catalytic activity due to the presence of palladium while the strong magnetic properties provided by the iron oxide shell enable facile catalyst recovery.

Magnetite (Fe₃O₄) nanoparticles have been the focus of a significant amount of recent research attention due to their promise in a range of applications including magnetic hyperthermia, magnetic particle

imaging (MPI), and as MRI contrast agents.^[1] Their applicability as catalysts has been less fully explored, despite the obvious advantages of being low-cost, non-toxic and environmentally benign. Magnetite nanoparticles have typically been used as magnetically active supports for heterogeneous or homogeneous catalysts.^[2] This introduces a second functionality to the catalyst in terms of a strong magnetic response that allows for simplified catalyst recovery post-reaction. A few recent studies have demonstrated that magnetite nanoparticles can be applied directly as hydrogenation catalysts; in particular, for the selective reduction of nitroarenes to anilines and for olefin and alkyne hydrogenations.^[3]

Combining two active species in close contact is an established approach to increase catalytic activity by introducing synergistic effects.^[4] Here, we expand on these efforts by forming Pd/Fe₃O₄ core-shell nanowire clusters and applying them as hydrogenation catalysts. Palladium is one of the cheaper platinum group metals, is a well-known hydrogenation catalyst, and can be grown in a wide range of nanoparticle shapes.^[5] It has a tendency to grow anisotropically, which we exploit to form thin (< 2 nm) Pd nanowires that self-assemble into agglomerated clusters. By reducing the dimensions of the nanowires to less than 10 nm, we approach the realm where catalytic activity is optimized.^[6] These nanowire clusters act as a high surface area framework that is then coated by the growth of a strongly magnetic iron oxide shell. The shell has the added benefit of protecting the palladium from losses due to leaching or sintering, a role that is typically provided by catalytically benign SiO₂ or CeO₂.^[6b, 7]

We then apply the nanostructures to a model hydrogenation reaction; acetophenone to 1-phenylethanol. This reaction is industrially important as 1-phenylethanol is a common precursor for the preparation of analgesic and anti-inflammatory drugs and due to its characteristic strawberry scent is used widely in the fragrance and food industries.^[8] We show that the addition of palladium substantially increases hydrogenation activity when compared to Fe/Fe₃O₄ core-shell nanoparticles, while still maintaining strong magnetic properties.

The Pd/Fe₃O₄ core-shell nanowire clusters are synthesized in a one-pot reaction by the continuous addition of precursor, which has previously been shown to give superior control over nanoparticle growth

via an Extended La Mer mechanism.^[1a] Briefly, triiron dodecacarbonyl ($\text{Fe}_3(\text{CO})_{12}$) and palladium acetate ($\text{Pd}(\text{OAc})_2$) were dissolved in dibenzyl ether in the presence of dodecylamine as surfactant. $\text{Fe}_3(\text{CO})_{12}$ is insoluble in most common high boiling point organic solvents, however upon mixing and gently heating with dodecylamine a soluble complex can be formed.^[9] The precursor solution was then continuously added via a syringe to a flask containing 1-octadecene and dodecylamine heated to 125 °C. Following the reaction, the nanostructures could be separated from solution with a simple bar magnet and purified for analysis, or applied as a catalyst in hydrogenation reactions.

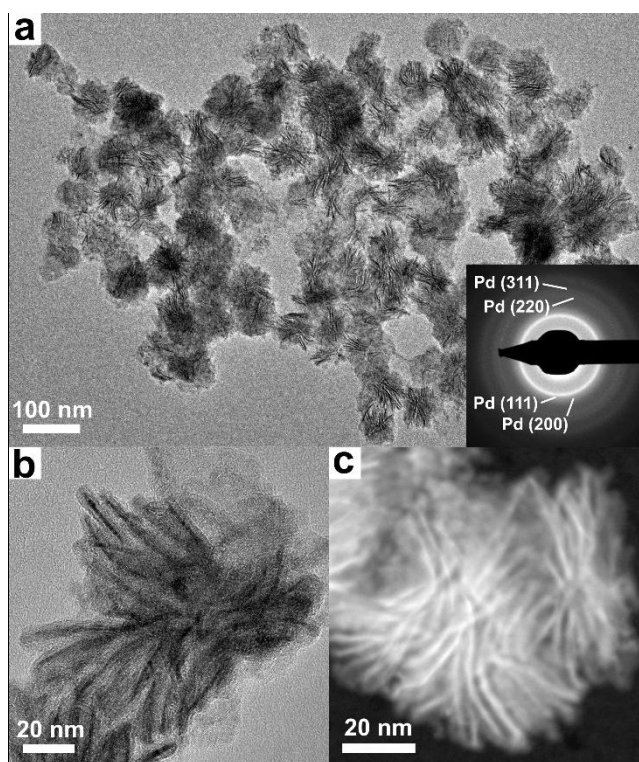


Figure 1. a) Transmission electron microscopy (TEM) analysis of the Pd/Fe₃O₄ core-shell nanowire clusters along with a selected area electron diffraction (SAED) pattern indicating the presence of the *fcc* crystal structure. b) High magnification TEM image of a single Pd/Fe₃O₄ core-shell nanowire cluster. The strong contrast difference indicates a Pd/Fe₃O₄ core-shell structure. c) High angle annular dark field (HAADF) imaging of a single nanostructure in which the areas of high Z-contrast confirm that palladium is confined to the wire cores.

The as-synthesized Pd/Fe₃O₄ core-shell nanowire clusters were imaged using transmission electron microscopy (TEM) and aberration corrected scanning transmission electron microscopy (AC-STEM) with the results shown in Figure 1. The Pd/Fe₃O₄ nanostructures are 71 ± 15 nm in size (Figure 1a, Figure S1) with a selected area diffraction (SAED) pattern (inset) indicating the presence of a face centered cubic (*fcc*) crystal structure, characteristic of palladium. The size was confirmed by DLS measurements (Figure S2) which also suggests that the structures are as-grown and stable in solution. High magnification TEM (Figure 1b, Figure S3) confirmed the nanostructures consisted of clusters of single crystalline *fcc* palladium nanowires coated in a polycrystalline shell of magnetite, Fe₃O₄. The polycrystalline structure and small grain size of the magnetite shell contributes to the diffuse rings observed in the SAED pattern. High angle annular dark field (HAADF) imaging (Figure 1c) showed a strong difference in Z-contrast confirming the Pd/Fe₃O₄ core-shell structure. The palladium wires were measured to have an average thickness of 1.7 ± 0.4 nm, which has previously been shown to be an optimal nanoparticle size for palladium hydrogenation catalysts.^[6c] To understand the growth of the Pd/Fe₃O₄ core-shell nanowire clusters we reduced the concentration of iron precursor by 5 x and investigated the effect this had on the resulting nanostructures (Figure S4). The palladium nanowires were observed to form self-assembled clusters; however, the growth of the iron oxide shell was incomplete. We also observed extensive faceting of the iron oxide shell which indicates its growth had become reaction limited.^[10] This suggests that formation of the Pd/Fe₃O₄ core-shell nanowire clusters begins with the self-assembly of palladium nanowires. Then, a high iron precursor concentration is required such that diffusion limited growth occurs leading to complete shell formation. To confirm, we attempted to decompose the iron precursor in the absence of Pd under the same reaction conditions. We observed no evidence of decomposition, confirming the palladium nanowires act as a site for the decomposition of the iron precursor and growth of the magnetite shell. Such behavior is consistent with a diffusion limited growth mechanism.^[1a]

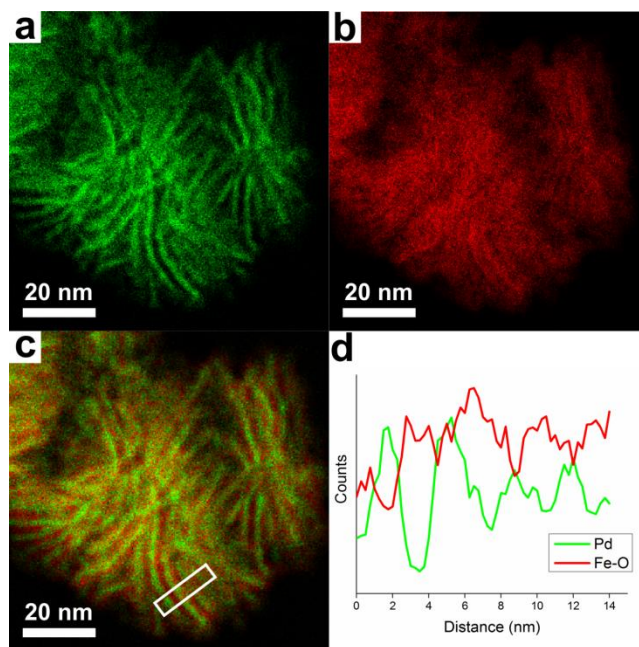


Figure 2. Spectral mapping experiments carried out using energy dispersive X-ray (EDX) spectroscopy in an AC-STEM. a) Pd and b) Fe-O signals. c) Combined image of the Pd and Fe-O signals overlaid confirming the core-shell structure. d) Line profile of the selected area in c).

Spectral mapping was then carried out using energy dispersive X-ray (EDX) spectroscopy in an aberration-corrected scanning transmission electron microscope (AC-STEM) (Figure 2). Figure 2a shows the EDX map for palladium, confirming that it is confined to the nanowire cores. The combined EDX map for iron and oxygen (Fe-O) is shown in Figure 2b. The distribution is much more uniform indicating a well-formed shell structure. Figure 2c shows the overlay of the two EDX maps, again confirming the core-shell structure. A line profile was extracted from the selected area in Figure 2c and is shown in Figure 2d. The palladium signal increases and decreases with a peak width of around 2 nm which is consistent with the thickness of the nanowire cores measured from HAADF imaging. The Fe-O line profile shows a similar behavior, albeit out of phase which indicates a core-shell structure.^[4b] The amplitude of the Fe-O signal is also decreased when compared to palladium which suggests it is more homogeneously distributed; as is expected for shell formation. Ensemble EDX measurements of the nanostructures gave an overall composition of 33 % palladium and 67 % magnetite (Figure S5).

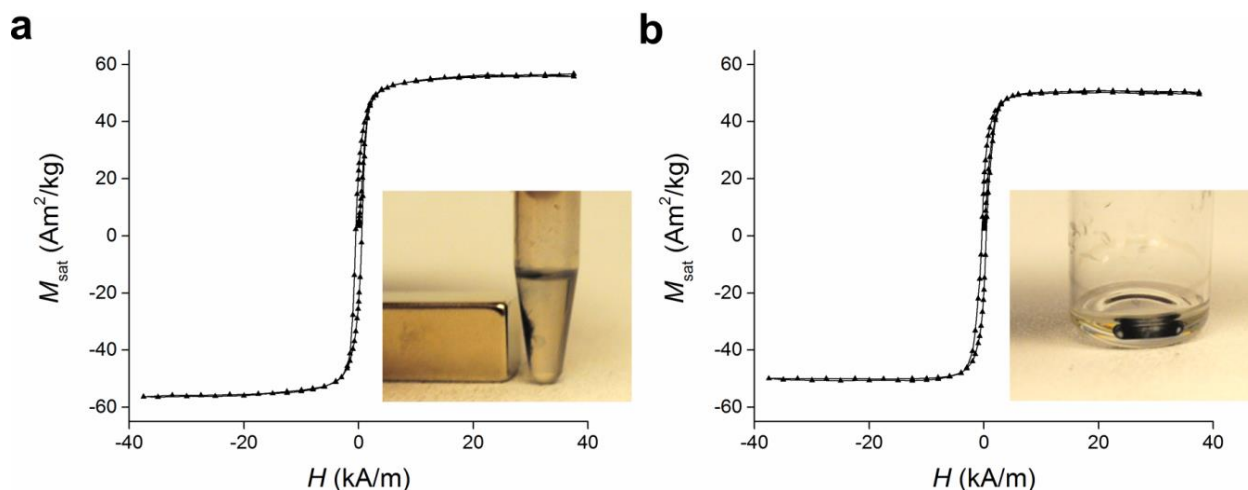


Figure 3. Results of superconducting quantum interference device (SQUID) measurements on the Pd/Fe₃O₄ core-shell nanowire clusters. a) Plot of magnetization (M) vs applied field (H) showing a saturation magnetization, M_{sat} , of 51 Am²/kg. (inset) Photo showing the separation of the nanostructures from the reaction solution using a simple bar magnet. b) Plot of magnetization (M) vs applied field (H) taken after the nanostructures have been applied in a hydrogenation reaction at 150 °C for 20 h. The nanostructures possess M_{sat} of 49 Am²/kg indicating they maintain their magnetic properties after being applied as a catalyst. (inset) Photo showing the nanostructures are attracted to a magnetic stir bar following the reaction, indicating facile catalyst recovery.

To investigate the magnetic properties of the Pd/Fe₃O₄ core-shell nanowire clusters, an aliquot of the nanoparticle solution was sealed under vacuum, and its magnetic response elucidated by means of superconducting quantum interference device (SQUID) magnetometry (Figure 3). The nanostructures possess a saturation magnetization, M_{sat} , of 51 Am²/kg of Pd/Fe₃O₄ @ 10 K (Figure 3a). This is a smaller value that can be typically achieved by isolated Fe₃O₄ nanoparticles (up to 80 Am²/kg), but represents a significant increase when compared to previously synthesized bimetallic magnetically active catalysts.^[1a]

^[1] The relatively high M_{sat} also demonstrates how the addition of palladium does not significantly affect the overall strength of the magnetic properties provided by magnetite. A field cooled zero-field-cooled (FC-ZFC) measurement gave a blocking temperature (T_{B}) of 206 K indicating the nanostructures are superparamagnetic at room temperature (Figure S6). This was confirmed by measuring the magnetization at 60 °C (Fig S7); no remanent magnetization was observed indicating the nanoparticles will be

superparamagnetic under typical catalysis conditions. This ensures they are stable in solution yet can be isolated post-reaction by simply placing the solution next to a bar magnet (Figure 3a, inset). Magnetic measurements were also performed after the nanostructures had been applied as hydrogenation catalysts at 150 °C for 20 h (*vide infra*). Upon cooling the reaction solution, the nanostructures were quickly attracted to the magnetic stir bar demonstrating facile catalyst recovery (Figure 3b, inset). The isolated nanostructures were then measured using SQUID magnetometry and found to possess an M_{sat} of 49 Am²/kg of Pd/Fe₃O₄ @ 10 K (Figure 3b), indicating the strong magnetic properties are maintained following their application as catalysts.

	Temperature (°C)	Conversion to 1-phenylethanol (%)	Conversion to (<i>R</i>)-1-phenylethanol (%)
Fe/Fe ₃ O ₄ Spherical Nanoparticles	60	24	14
Fe/Fe ₃ O ₄ Spherical Nanoparticles	150	42	24
Pd/Fe ₃ O ₄ Core-Shell Nanowire Clusters	60	34	62
Pd/Fe ₃ O ₄ Core-Shell Nanowire Clusters	150	64	84

Table 1. Results comparing the performance of magnetically recoverable catalysts for the hydrogenation of acetophenone to 1-phenylethanol. The as-synthesized Pd/Fe₃O₄ core-shell nanowire clusters were compared to spherical Fe/Fe₃O₄ nanoparticles that were also synthesized using dodecylamine as the surfactant. Reactions were carried out with 2 mol % loading of catalyst pressurized under 20 bar of H₂ for 20 h.

The Pd/Fe₃O₄ core-shell nanowire clusters were then tested for catalytic activity by applying them to the hydrogenation of acetophenone to 1-phenylethanol (Table 1). Activity was compared to another magnetically recoverable nanostructure catalyst; spherical Fe/Fe₃O₄ core-shell nanoparticles, which have previously been shown to be effective for olefin hydrogenation.^[3a] The spherical Fe/Fe₃O₄ nanoparticles were 10.8 ± 0.9 nm in size and were also synthesized using dodecylamine as the surfactant (for TEM see Figure S8).^[12] Thermogravimetric analysis (TGA) showed that both nanoparticle species possessed similar concentration of organic stabilizer in solution (Figure S9). This ensures any difference in catalytic performance is purely due to structural and compositional differences. For each catalytic reaction the nanoparticles were isolated by magnetic separation and washed with hexane before being loaded into a pressure reaction vessel along with neat acetophenone. Hydrogenations were carried out with 2 mol % catalyst loading pressurized under 20 bar H₂ for 20 h. The spherical Fe/Fe₃O₄ nanoparticles gave conversions of 24 % and 42 % at 60 °C and 150 °C, respectively. When the Pd/Fe₃O₄ core-shell nanowire clusters were applied as catalysts the conversion efficiencies increased significantly to 34 % and 64 % at 60 °C and 150 °C, respectively. These values represent a significant increase in the activity of magnetically recoverable nanostructures for acetophenone hydrogenation. Kelsen et al reported a conversion of 4 % using ultrasmall iron nanoparticles at room temperature and Karimi et al showed a conversion of 7 % at 90 °C when a palladium species was added to the surface of Fe₃O₄ nanoparticles.^[11d, 13] This increase in activity is most likely due to a combination of the complex shape of the Pd/Fe₃O₄ core-shell nanowire clusters, as well as the introduction of Pd to the system. No common side products (e.g., ethylbenzene, cyclohexylmethylketone) were observed indicating the Pd/Fe₃O₄ core-shell nanowire clusters were selective for the formation of 1-phenylethanol (Figure S10).^[8c] TEM analysis was performed following catalysis which showed that the nanostructures maintained their core-shell nanowire cluster morphology (Figure S11). Investigation into the enantioselectivity of the different catalysts is also required due to the presence of a chiral center on 1-phenylethanol. Industrially, (*R*)-1-phenylethanol is preferred due to its mild floral odor and use as an ophthalmic preservative and cholesterol absorption inhibitor.^[14] The Fe/Fe₃O₄ nanoparticles were observed to produce predominantly (*S*)-1-phenylethanol, with percent conversion to

(*R*)-1-phenylethanol of only 14 % and 24 % at 60 °C and 150 °C, respectively (Figure S12). Conversely the Pd/Fe₃O₄ core-shell nanowire clusters produced much larger percent conversion to (*R*)-1-phenylethanol; yielding 62 % and 84 % at 60 °C and 150 °C, respectively. These results indicate the Pd/Fe₃O₄ core-shell nanowire clusters are promising candidates for selective and magnetically recoverable hydrogenation catalysts.

In summary, we have grown Pd/Fe₃O₄ core-shell nanowire clusters from the continuous addition of precursor in a thermal decomposition method. The nanostructures form when thin palladium nanowires self-assemble into clusters which act as a high surface area framework for the growth of a magnetite shell. The nanostructures display significantly increased activity for the hydrogenation of acetophenone to 1-phenylethanol when compared to Fe/Fe₃O₄ core-shell nanoparticles. The strong magnetic properties are maintained after the completion of the catalytic reaction, allowing for facile catalyst recovery by magnetic separation.

Experimental Section

Materials

Triiron dodecacarbonyl (Fe₃(CO)₁₂), palladium acetate (Pd(OAc)₂), dodecylamine, 1-octadecene, dibenzyl ether, and acetophenone were all purchased from Sigma-Aldrich. Solvents were dried and degassed before use.

Synthesis of Pd/Fe Nanowire Clusters

A 10 mL reaction flask was charged with 1-octadecene (3 mL) and dodecylamine (100 mg, 0.56 mmol). This was transferred to an air-free Schlenk line and heated to 125 °C under a nitrogen atmosphere. The reaction solution was prepared by adding together Fe₃(CO)₁₂ (17.5 mg, 0.035 mmol), Pd(OAc)₂ (10 mg, 0.045 mmol), dodecylamine (250 mg, 1.3 mmol) and dibenzyl ether (5 mL) under an inert atmosphere. This was heated to 75 °C, with stirring, to dissolve the metal precursors. A 5 mL aliquot of the reaction solution was then taken up in a syringe and injected into the reaction flask (kept at 125 °C) at a rate of 33 μL/min.

The reaction was aged for 120 min at 125 °C following the completion of the drip. The reaction was then cooled to room temperature and transferred back into a nitrogen-filled glove box. The magnetic stir bar was removed from the product, and the latter was resuspended in pure 1-octadecene for SQUID analysis. For size characterization, an aliquot was taken for HRTEM and AC-STEM analysis. This was then purified by washing three times with chloroform and isopropanol before being suspended in chloroform.

Characterization

HRTEM samples were prepared by dropcasting the dispersion onto a carbon coated copper grid. Bright field images were collected using a Philips Tecnai HRTEM operating at 300 keV. HAADF images and EDX elemental mapping were performed using an FEI Company Titan G2 80 – 200 AC-STEM operated at 200 kV and equipped with the X-FEG (an ultrastable high-brightness Schottky FEG source), Super-X EDX detector system (four windowless silicon drift detectors with a combined solid angle of 0.7 sr), and a spherical aberration corrector (CEOS DCOR) on the probe-forming optics. Magnetization measurements were collected using a Quantum Design MPMS-7 SQUID magnetometer. Samples were prepared by depositing a small amount of the synthesized nanoparticles suspended in 1-octadecene and vacuum sealing in a NMR tube. Magnetization curves were recorded at 10K. The precise iron mass of each sample was determined destructively by heating the sample in a 600°C furnace for 1 hour to incinerate the organic material and then dissolving the iron containing residue in hydrochloric acid. A phenanthroline/Fe²⁺ complex was formed in solution and spectrophotometrically quantified. Magnetic saturation is then reported as Am²/kg Pd/Fe₃O₄, as determined by EDX analysis. Zero-field cooled (ZFC) magnetization curves were obtained by cooling the sample to 4 K with no applied field, then applying a field of 10 Oe (0.8 kA/m), and recording the magnetization from 4 K to 250 K. With the 10 Oe field still applied, the sample was then cooled from 250 K to 4 K to obtain the field-cooled (FC) magnetization. TGA was carried out by heating an alumina crucible containing nanoparticles to 600 °C in a Netzsch STA 449 *FI* Jupiter instrument.

Hydrogenation Reactions

Hydrogenation reactions were performed using a 300 mL General Purpose Parr Reaction Vessel (Model No. 4766). Briefly, the nanostructures were magnetically separated from solution and washed with hexane before being added in a vial with neat acetophenone to give a 2 mol % catalyst loading. This was then placed in the Parr reactor and pressurized with 20 bar H₂. The reactor was set in a silicon oil bath and heated to the desired temperature where it was left to react for 20 h. Following the completion of the reaction the nanostructures were isolated by magnetic separation and the hydrogenation product analyzed using ¹H NMR on an Anasazi EFT 90 MHz instrument. Hydrogenation yield was confirmed by integrating the respective methyl peaks for acetophenone and 1-phenylethanol and applying the values to a calibration curve.

Acknowledgements

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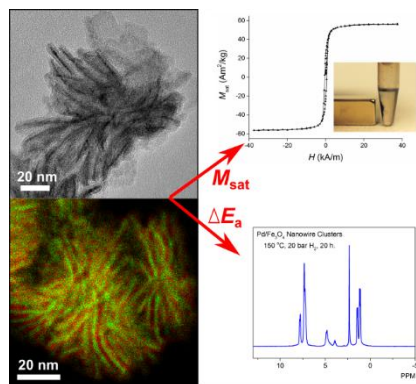
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TOC:



Catalytically active Pd/Fe₃O₄ core-shell nanowire clusters have been synthesized via the self-assembly of thin palladium nanowires followed by the growth of a magnetically active iron oxide shell. The nanostructures are applied as hydrogenation catalysts for the conversion of acetophenone to 1-phenylethanol; demonstrating increased activity, enantioselectivity and facile catalyst recovery using magnetic separation.

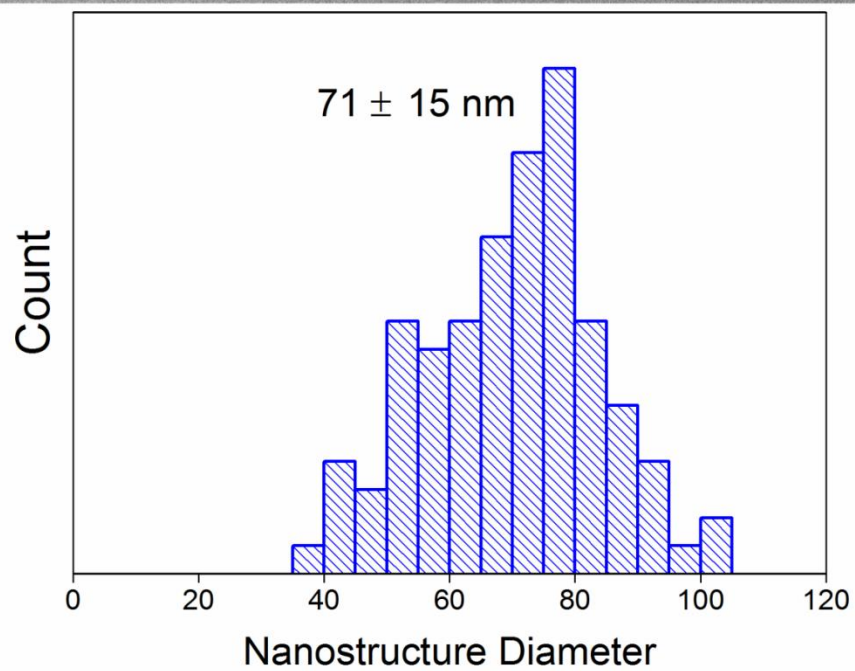
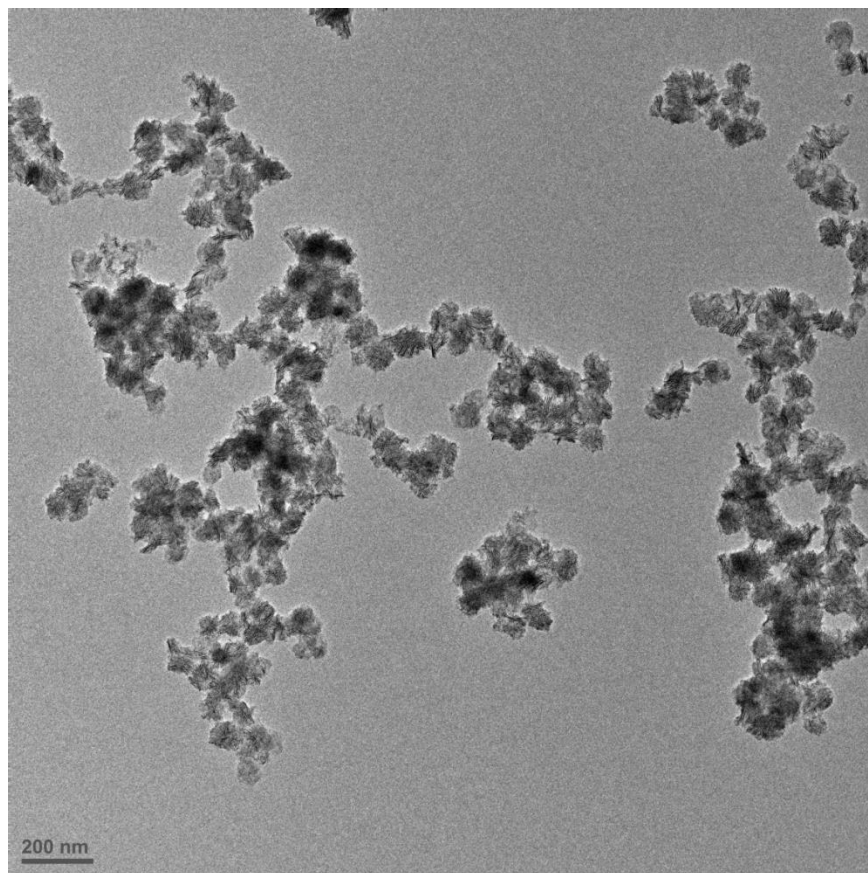


Figure S1. Transmission electron microscopy (TEM) images of the Pd/Fe₃O₄ core-shell nanowire clusters and corresponding size analysis (71 ± 15 nm).

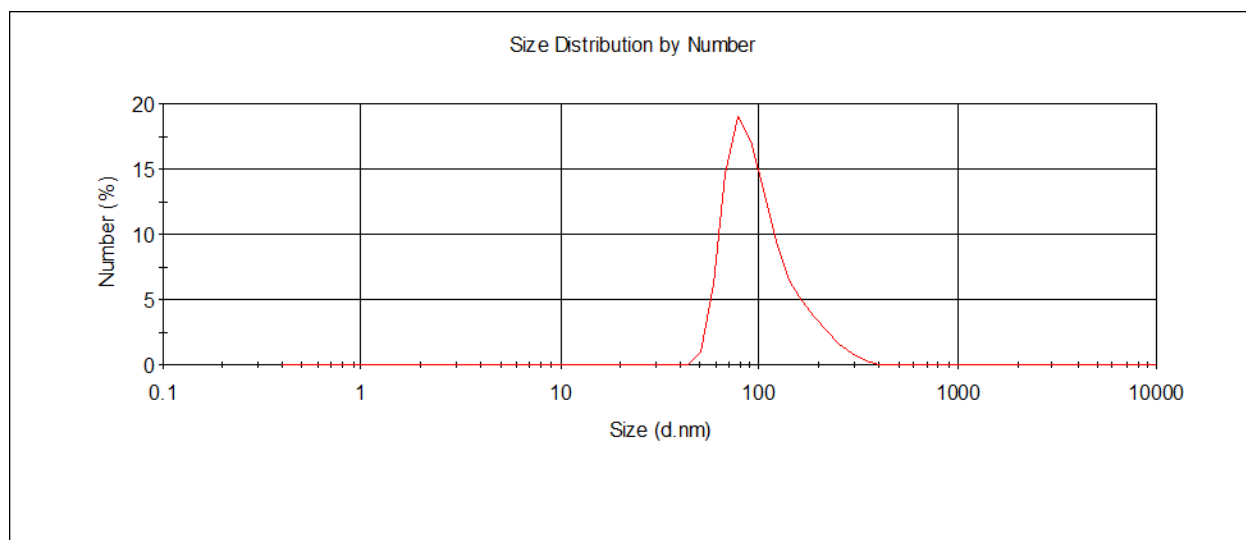


Figure S2. Dynamic light scattering (DLS) measurements confirming the size of the nanostructures (median size = 78.8 nm). DLS also indicates that the nanostructures are as-grown and stable in solution.

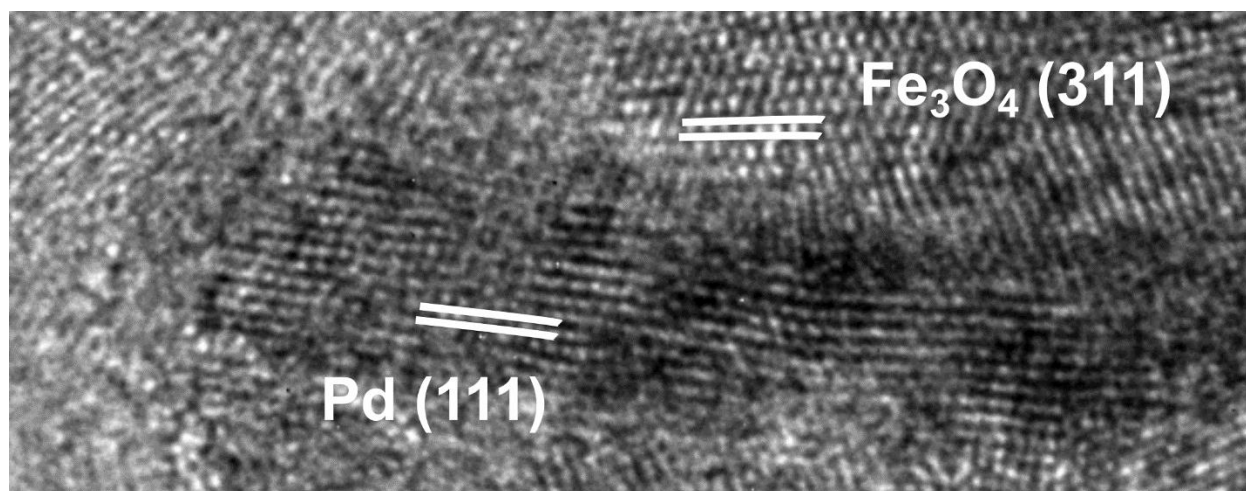


Figure S3. High resolution transmission electron microscope (HRTEM) image showing visible lattice plans of *fcc* Pd overgrown with a magnetite shell. There are no visible twin planes or defects in the Pd nanowire indicating a single crystalline structure. The magnetite shell, on the other hand shows multiple defects, indicating a polycrystalline structure.

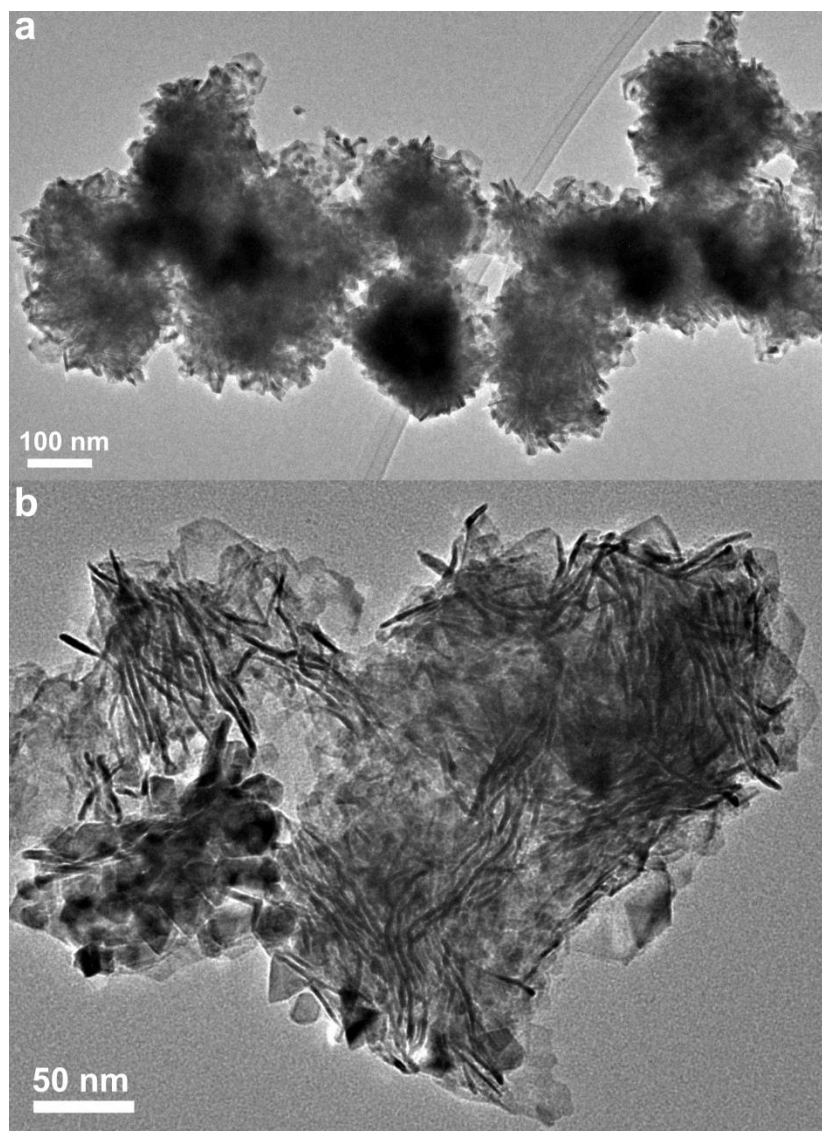


Figure S4. TEM analysis of Pd/Fe₃O₄ core-shell nanowire clusters synthesized with iron precursor concentration reduced by 5 x.

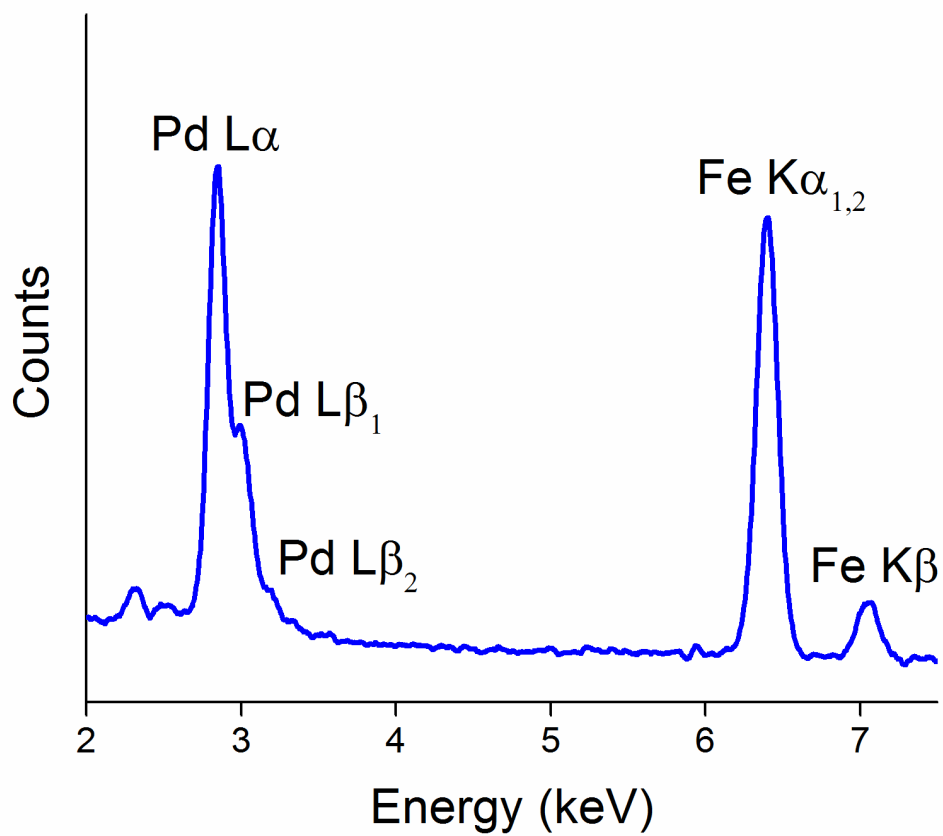


Figure S5. Energy dispersive X-ray spectroscopy analysis of a large ensemble of Pd/Fe₃O₄ core-shell nanowire clusters. Quantitative analysis gave a composition of 33 % Pd and 67 % Fe₃O₄.

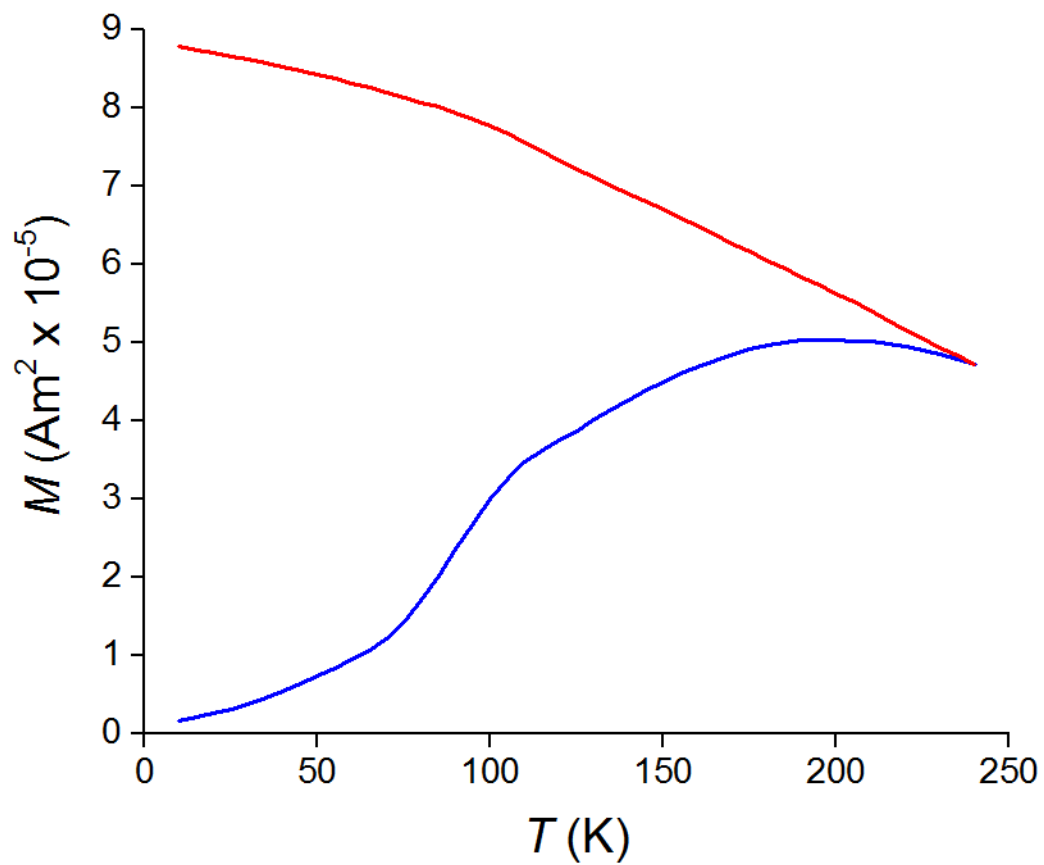


Figure S6. Zero-field cooled (ZFC) curve for Pd/Fe₃O₄ core-shell nanowire clusters showing a blocking temperature, T_B , at 206 K indicating the nanostructures are superparamagnetic at room temperature.

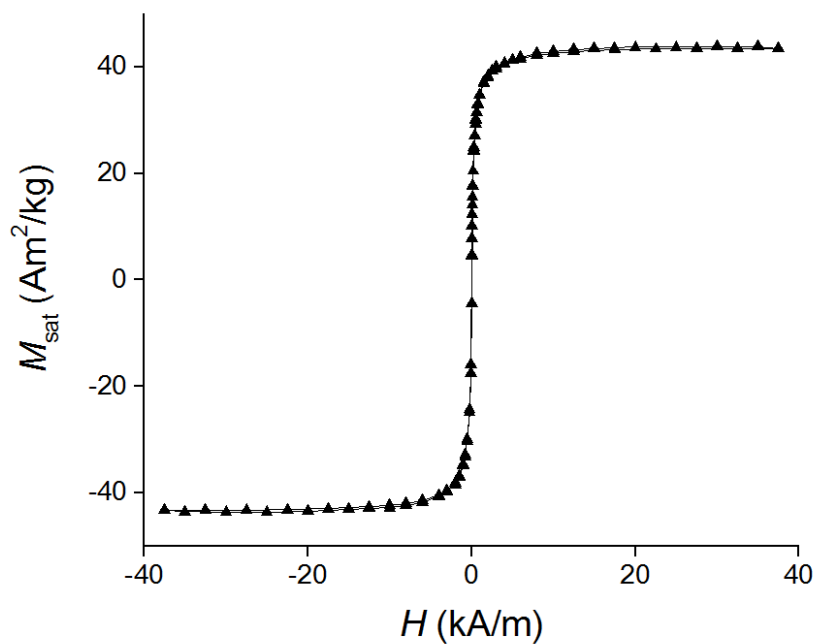


Figure S7. Results of superconducting quantum interference device (SQUID) measurements on the Pd/Fe₃O₄ core-shell nanowire clusters carried at 60 °C. A plot of magnetization (M) vs applied field (H) gave a saturation magnetization of 44 Am^2/kg , which as expected, is a slight decrease when compared to the measurement taken at 10 K. No noticeable magnetic remanence was observed confirming the nanostructures are superparamagnetic.

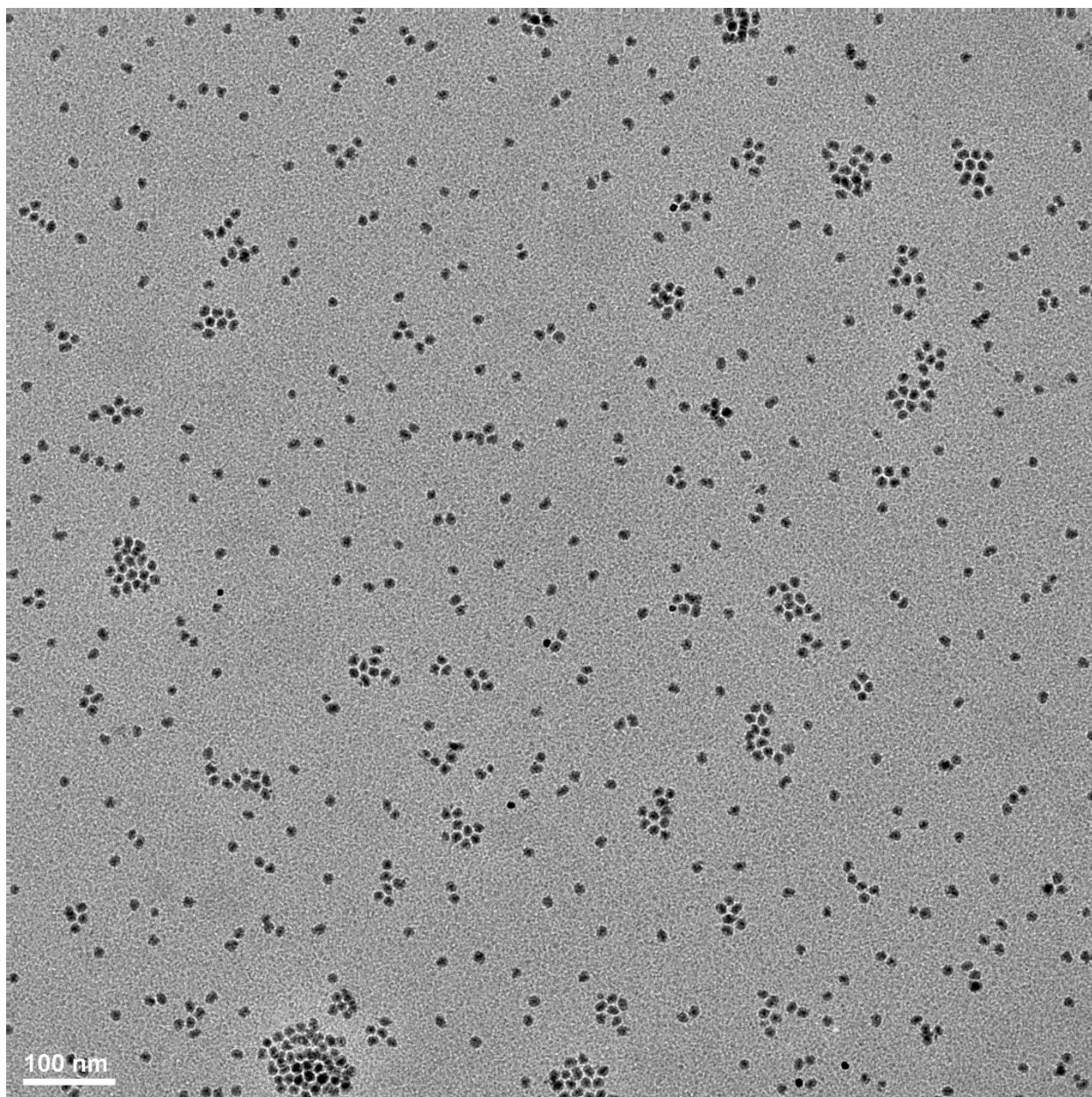


Figure S8. Spherical Fe/Fe₃O₄ nanoparticles 10.8 ± 0.9 nm in size also synthesized using dodecylamine as the surfactant and then applied as hydrogenation catalysts. Forming these nanoparticles with the same precursor and surfactant ensures any difference in catalytic performance is purely due to structural and compositional differences when compared to the Pd/Fe₃O₄ nanostructures.

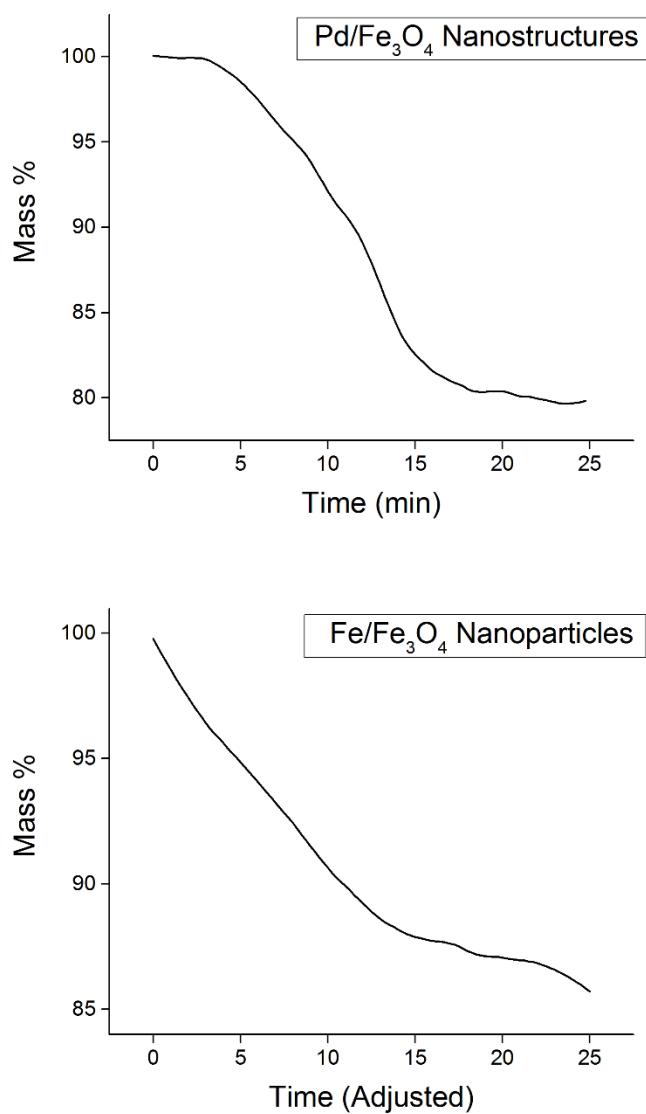


Figure S9. Thermogravimetric analysis (TGA) of the as synthesized Pd/Fe₃O₄ core-shell nanowire clusters and the Fe/Fe₃O₄ core-shell nanoparticles. Samples were heated to 600 °C in alumina crucibles to investigate the content of DDA stabilizer on the surface of the nanostructures. The Pd/Fe₃O₄ core-shell nanowire clusters possess a stabilizer content of ~18 % whereas the Fe/Fe₃O₄ core-shell nanoparticles possess a stabilizer content of ~14%.

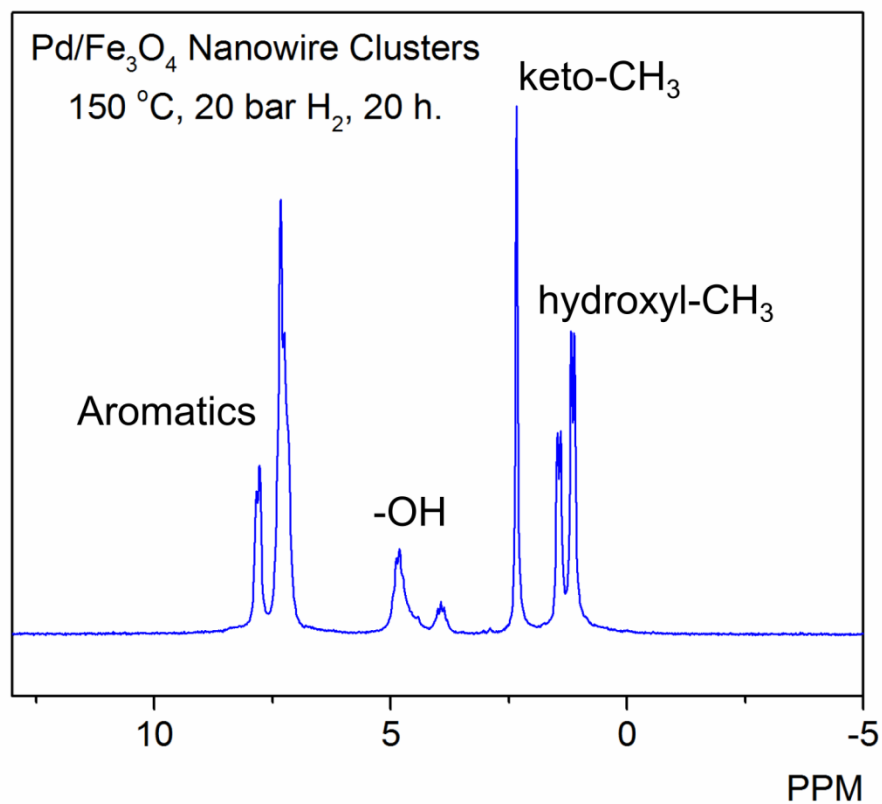


Figure S10. Nuclear magnetic resonance (NMR) spectroscopy performed on the reaction solution following the hydrogenation of acetophenone in the presence of Pd/Fe₃O₄ core-shell nanowire cluster at 150 °C under 20 bar H₂, for 20 h. No common side products were observed indicating strong selectivity.

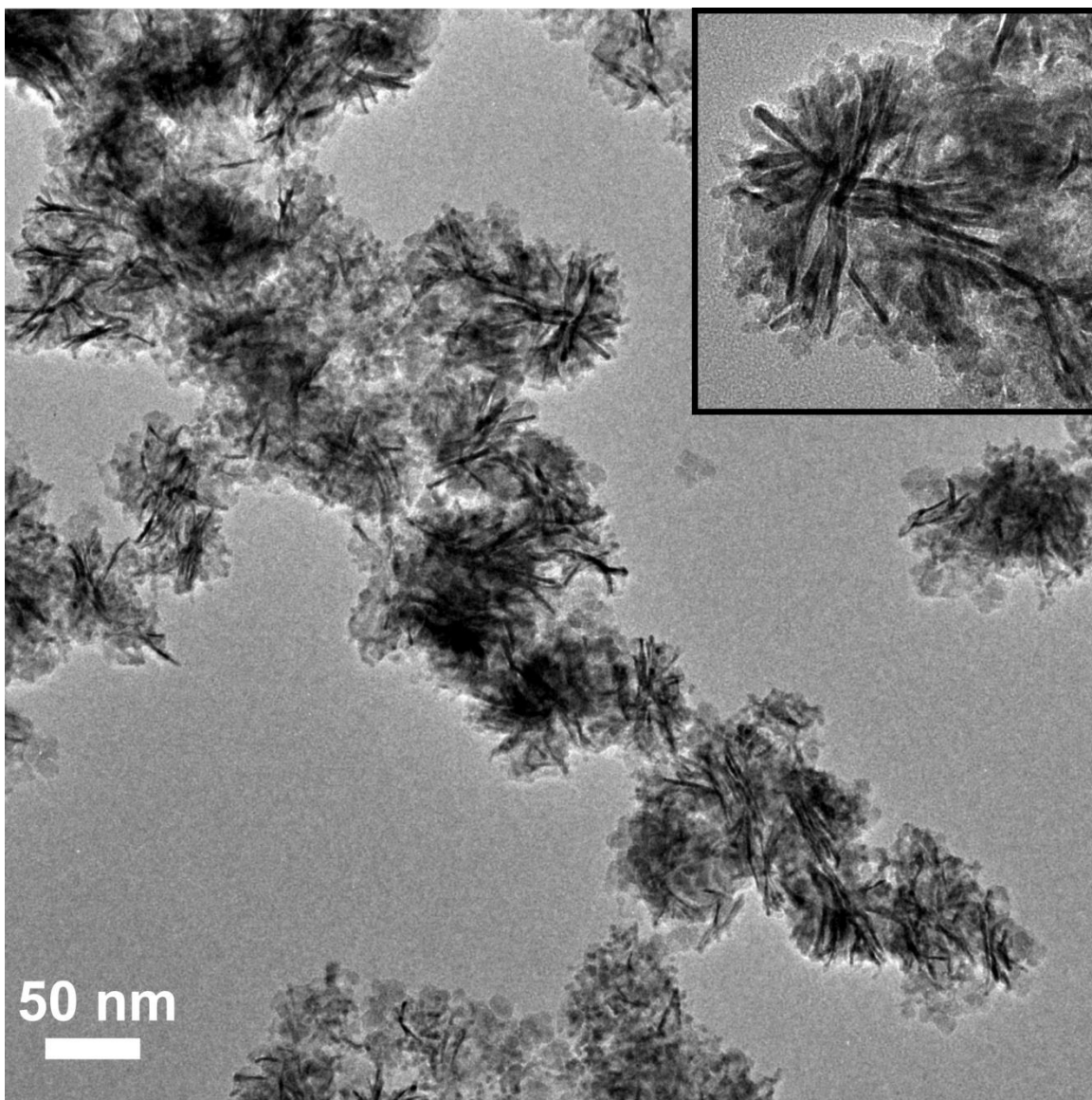


Figure S11. TEM analysis of Pd/Fe₃O₄ core-shell nanowire clusters following their application as hydrogenation catalysts at 150 °C under 20 bar H₂ for 20 h.

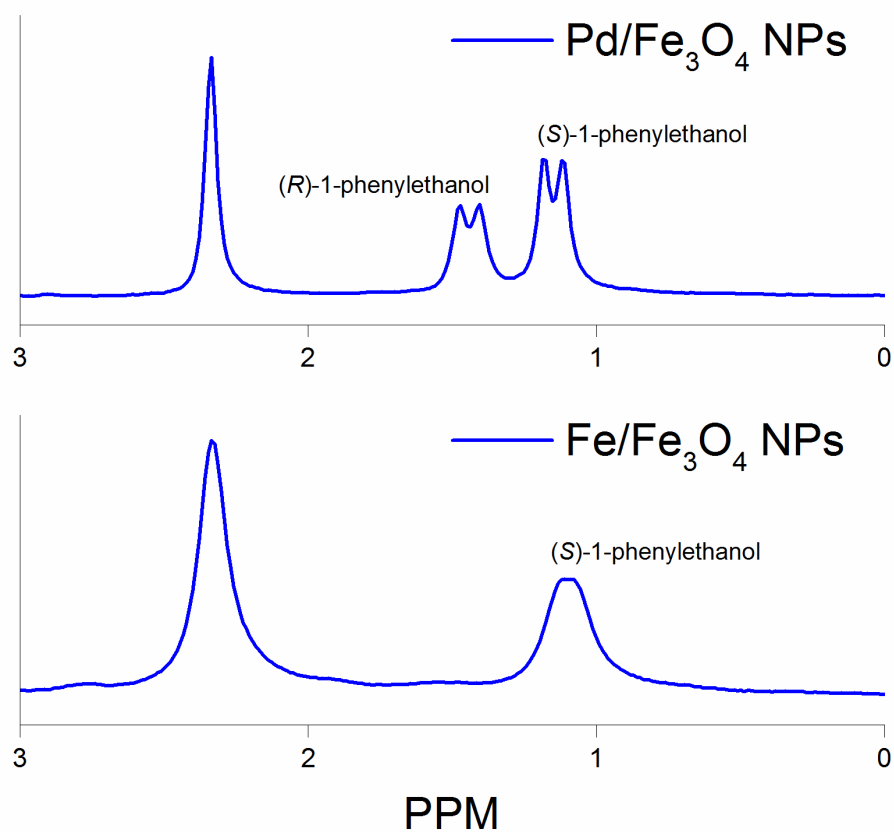


Figure S12. NMR measurements showing the difference in enantioselectivity of the Pd/Fe₃O₄ core-shell nanowire clusters and the Fe/Fe₃O₄ spherical core-shell nanoparticles after hydrogenations were carried out at 150 °C.