

Seed-Mediated Synthesis of Palladium Nanorods and Branched Nanocrystals and Their Use as Recyclable Suzuki Coupling Reaction Catalysts

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Abstract: In this study, we have used a simple seed-mediated synthesis process to prepare uniform Pd nanorods with average lengths of ~200 and 300 nm through the addition of 50–100 μL of 0.004 M copper acetate solution into the growth solution for the first time. Because of their long lengths, they nicely settled to the bottom of the reaction vial and can easily be separated from the suspended faceted particles. The nanorods have an average diameter of ~20 nm, so they have high aspect ratios of 10–15 or more. They can readily self-assemble into high-density packing structures on substrates. By increasing the volume of the copper acetate solution added to 250 μL , extensively branched Pd nanocrystals were obtained. The crystal structures of both particle morphologies have been examined. The nanorods possess a pentatwinned structure. Different growth directions have been found for the branched nanocrystals. The growth mechanism of these nanostructures was studied in great detail. A mixture of short Pd rods and faceted particles was formed first and elongated into long rods or branched nanocrystals with the assistance of copper atom deposition. A reduction potential of copper lower than that of palladium leads to periodic deposition and reoxidation of copper atoms on the growing rods and faceted particles. Use of other metal ions did not form long nanorods and branched nanocrystals. UV–vis spectra of the 200 nm Pd nanorods showed a significant absorption band in the near-infrared region with band maximum at ~1800 nm, while the 300 nm rods have band maxima of 2000–2100 nm. Both the nanorods and branched nanocrystals were found to serve as highly efficient and recyclable catalysts for catalyzing a Suzuki coupling reaction between phenylboronic acid and iodobenzene. They are also thermally stable under the reflux condition and can be easily removed from the product solution. These novel Pd nanostructures should find use in other palladium-catalyzed reactions.

Introduction

Palladium is an important metal for catalyzing many organic reactions such as Suzuki, Heck, and Stille coupling reactions.^{1,2} In recent years, there is a growing interest to prepare Pd nanostructures with morphological control. For example, Xia et al. have successfully used a water-based or a mixed polyol/water system in the presence of poly(vinyl pyrrolidone) (PVP) to make a variety of Pd nanostructures such as nanobars, short nanorods, nanocubes, octahedra, icosahedra, and nanoplates.^{3–5} In other reports on the synthesis of structurally well-defined Pd nanostructures, a water-based system with cetyltrimethylammonium bromide (CTAB) added as the capping surfactant has been used to prepare Pd nanocubes, short nanorods, and multiply twinned particles.^{6–9} Despite the early success, it remains challenging to synthesize relatively long Pd nanorods with lengths on the order of 150–350 nm in high yield. In the few reports describing the formation of Pd nanorods, the rods are

typically less than 150 nm in length, and they cannot be easily separated from the cubic byproducts.^{5,6,9} Recently, a hydrothermal synthesis approach for the production of Pd nanowires and nanorods has been described.¹⁰ A mixture of PdCl₂, PVP, NaI, and water was heated to 200 °C for 8 h to form Pd nanorods with a uniform diameter of 19 nm and an aspect ratio of ~6. Although Pd nanorods can be made in high yield, the energy cost may be high. To prepare relatively long Pd nanorods, it is still desirable to develop a simple seed-mediated growth procedure similar to that used to make high aspect ratio gold nanorods.¹¹ Previously, we have adopted this process to grow high aspect ratio gold nanorods with a high yield.¹² Here we report the seed-mediated synthesis of Pd nanorods and branched

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nanocrystals. Uniform Pd nanorods with average lengths of ~200 and 300 nm have been successfully prepared in high yield. We discovered that the addition of a small amount of copper ion source such as copper acetate to the growth solution was the key to the generation of Pd nanorods with these lengths. The rod length can be tuned by adjusting the amount of copper acetate introduced into the growth solution. Using this simple control, novel Pd nanocrystals with extensively grown thin branches were also obtained. We have characterized the crystal structures and optical properties of these Pd nanostructures. The growth mechanism of these Pd nanostructures with respect to the role of the copper ion source has been studied and is proposed here.

Pd nanoparticles of just a few nanometers in size have been demonstrated to be efficient catalysts for Suzuki coupling reactions.^{13–17} Hollow Pd spheres composed of ~10 nm Pd nanoparticles have also been shown to exhibit a high catalytic efficiency for Suzuki coupling reactions even after multiple cycles.¹⁸ Since Pd nanorods have never been tested for their application as catalysts for Suzuki coupling reactions, we have examined the possibility of using these Pd nanorods and branched nanocrystals to catalyze the coupling reaction between phenylboronic acid and iodobenzene. Remarkably, both Pd nanostructures gave high product yields even after three cycles of reaction, suggesting that even large Pd nanocrystals can also serve as excellent and recyclable catalysts. Because of their relatively large sizes, they can be easily separated from the product solution. The Pd nanocrystals are also thermally stable; they did not show appreciable change in morphology after the reaction.

Experimental Section

Synthesis of Palladium Seeds. First, a 2.0 mM PdCl₄²⁻ solution was prepared by dissolving 0.0355 g of deep brown PdCl₂ powder (Aldrich, 99%) and 0.876 g of NaCl in 100 mL of deionized water. The initial brick red solution turned to an orange solution as the powder was completely dissolved. In a round-bottom flask, 10 mL of 2.5 × 10⁻⁴ M PdCl₄²⁻ aqueous solution, prepared by diluting the 2.0 mM PdCl₄²⁻ solution, was bubbled with nitrogen for 30 min to remove the dissolved oxygen and prevent reoxidation of the initially formed seed particles. The bubbled solution was injected into a two-neck flask containing 0.3645 g (1 mmol) of cetyltrimethylammonium bromide (CTAB) surfactant (Alfa Aesar, 98%) and stirred until the CTAB powder was dissolved. Concurrently, 10 mL of ice-cold 0.015 M NaBH₄ (Aldrich, 98%) solution was prepared in another flask. Next, 220 μL of the NaBH₄ aqueous solution was injected into the solution in the two-neck flask. The resulting solution turned dark brown upon the addition of NaBH₄, indicating the formation of Pd seeds. This solution must be kept under nitrogen to avoid exposure to air.

Synthesis of Palladium Nanorods with an Average Length of 308 nm. Two 20 mL vials labeled A and B were used. The growth solution was prepared by adding 0.345 g of CTAB powder and 10 mL of 2.5 × 10⁻⁴ M PdCl₄²⁻ solution into both of these vials and stirred until the CTAB powder was completely dissolved. The solution gives a pale orange color. Then 78 μL of 0.1 M L-(+)-ascorbic acid (Riedel-de-Haën, 99.7%) was added as a reducing

agent into vial A. Next, 84 μL of the seed solution was transferred into vial A, and the vial was shaken for 5 s. After 2 h, the solution in vial A turned blackish green. At this time, 100 μL of 4.0 × 10⁻³ M copper(II) acetate (J.T. Baker, 98%) solution was added to vial B, followed by the addition of 78 μL of 0.1 M L-(+)-ascorbic acid. A volume of 84 μL of the blackish green solution in vial A was withdrawn and added to vial B. Again, this vial was shaken for 5 s. The mixture was left undisturbed at 30 °C for 20 h, and the solution turned dark brown. After decanting the solution which contains mostly spherical or faceted Pd nanoparticles, a black precipitate was observed at the bottom of the vial. The black precipitate was found to be Pd nanorods with an average length of 308 nm. To collect the product, 6 mL of deionized water was added to the precipitate and the solution was subject to centrifugation at 6500 rpm for 16 min (Hermle Z323 centrifuge). The top solution was withdrawn with a pipet. To ensure the removal of the surfactant, the precipitate was redispersed in 6 mL of deionized water and centrifuged at 6800 rpm for 16 min. A simple illustration of the procedure used here is shown in Scheme 1.

Synthesis of Palladium Nanorods with an Average Length of 200 nm. The procedure used here is the same as that described above, except with the addition of only 50 μL of 4.0 × 10⁻³ M copper(II) acetate solution into vial B.

Synthesis of Branched Palladium Nanocrystals. The synthetic procedure used here is the same as that described for the growth of Pd nanorods with an average length of 308 nm, except with the addition of 250 μL of 4.0 × 10⁻³ M copper(II) acetate solution into vial B and the use of a reaction time of 24 h. The solution turned dark blue, and the precipitate was similarly collected by centrifugation.

Use of Pd Nanorods and Branched Nanocrystals as Suzuki Coupling Reaction Catalysts. The Suzuki coupling reaction between phenylboronic acid and iodobenzene was performed using the Pd nanorods with an average length of 308 nm and branched nanocrystals as catalysts. First, 0.243 g (2 mmol) of phenylboronic acid, 0.921 g (4 mmol) of K₃PO₄, and 1 mL of the Pd nanostructure solution were added to 5 mL of ethanol/water mixture with a volume ratio of 4:1. Specifically, 1 mL of the Pd nanostructure solution contained 1.8 mg of Pd nanorods (1.6 mol % of the limiting reagent iodobenzene) or 2.0 mg of branched Pd nanocrystals (1.8 mol % of iodobenzene). This amount of Pd nanorods was obtained by combining the nanorods produced from 40 sample vials (or 20 sample vials for the branched nanocrystals). The mixture was heated to 85 °C under reflux, and then 112 μL (1 mmol) of iodobenzene was added. The reaction time was 4 h. After the reaction, the product was extracted with CH₂Cl₂, and the Pd particles were removed by filtration. The product was subsequently purified by column chromatography on silica using an ethyl acetate/hexane mixture with a volume ratio of 1:19 as the eluent. Finally, the biphenyl product was analyzed by gas chromatography and low-resolution mass spectroscopy (GC–MS). Selected GC–MS *m/z* results and the relative peak intensities are given here: 154 (M⁺, 100), 153 (40), 77 (7), 76 (15), and 51 (7). The GC–MS spectrum is consistent with the reported data.¹⁹

Recyclability Tests of the Catalysts for Suzuki Coupling Reaction. To simplify the reaction and avoid the loss of the Pd nanostructure catalysts for the recyclability tests, fresh reagents were added to the same reaction solution. For each recycle, 1 mmol of iodobenzene and 1 mmol of phenylboronic acid were added. The mixture was also refluxed at 85 °C for 4 h.

Instrumentation. Transmission electron microscopy (TEM) characterization was performed on a JEOL JEM-2100 microscope with an operating voltage of 200 kV. Scanning electron microscopy (SEM) images of the samples were obtained using a JEOL JSM-7000F electron microscope. Energy-dispersive spectroscopy (EDS) mapping images were acquired on another JEOL JEM-2100 electron

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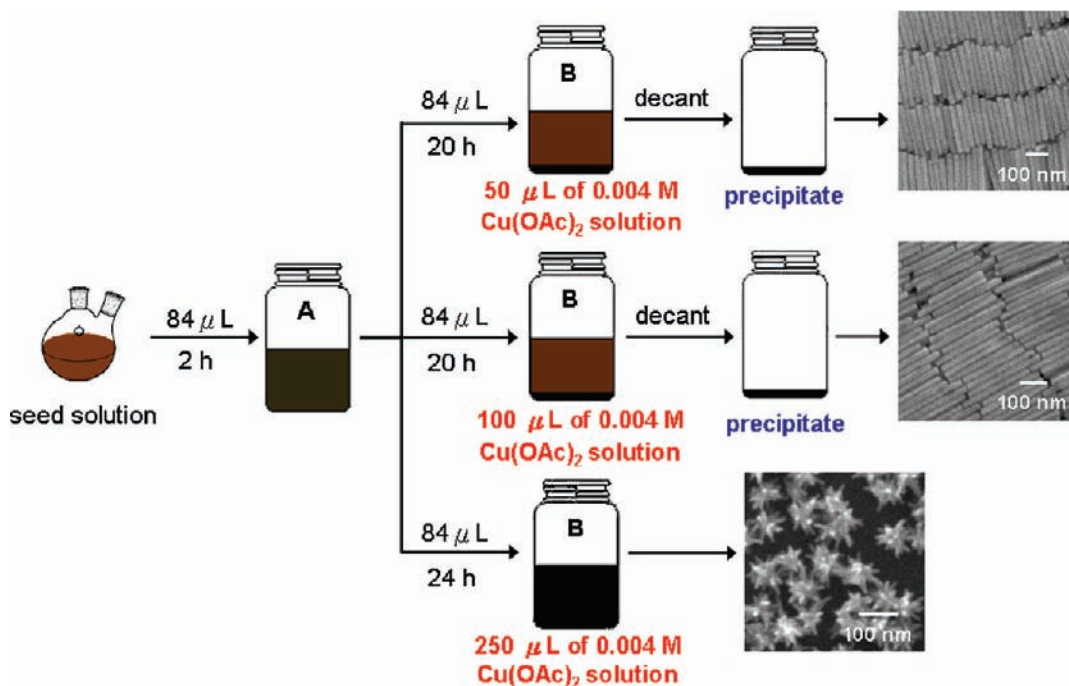
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Scheme 1. Experimental Procedure Used to Make the Palladium Nanorods and Branched Nanocrystals (The Colors Shown are the Final Colors Observed for These Solutions)



microscope equipped with a STEM unit and an Inca Energy 250 detector from Oxford Instruments. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer with Cu K α radiation. UV–vis absorption spectra were taken using a JASCO V-570 spectrophotometer. GC–MS analysis was performed on an Agilent Technology 6890N Network GC system equipped with an Agilent 5973 Network mass selective detector and a HP-1 capillary column.

Results and Discussion

In this study, the Pd nanorods and branched nanocrystals were synthesized by a two-stage seeding growth process (see Scheme 1). Short Pd nanorods were first grown in vial A for 2 h. Long nanorods and branched nanocrystals were obtained after further growth in vial B for 20 or 24 h. The reaction time is long because the nanorod growth is relatively slow. A big advantage of keeping the solution undisturbed during this growth period is that the long nanorods settle nicely to the bottom of vial B to form a precipitate, and thus the nanorods can be easily separated from the faceted particles suspended in the solution. Figure 1 shows the SEM images of the Pd nanorods synthesized by adding 50 and 100 μL of 0.004 M $\text{Cu}(\text{OAc})_2$ solution into the growth solution in vial B and their length distribution plots. Table 1 gives their average lengths and standard deviations. Simply by increasing the volume of $\text{Cu}(\text{OAc})_2$ added from 50 to 100 μL , the average rod length can be tuned from ~ 200 to 300 nm. With an average rod diameter of ~ 20 nm, the Pd nanorods have high aspect ratios of 10–15 and can be as high as ~ 18 . Because of their highly uniform dimensions, they can readily self-assemble into long-range-ordered side-by-side and end-to-end packing structures over multiple layers on substrates. Remarkably, such high-density packing structures can extend over very large areas (10 μm^2 regions or more). Because of their longer lengths, we found that the 300 nm rods are more likely to exhibit some directional alignments over long ranges (see Supporting Information Figure S1). The formation of such a large amount of long Pd nanorods offers the exciting

opportunities for the investigation of their physical properties and potential applications.

Further structural characterization of the Pd nanorods was conducted. Their XRD pattern matches well with that of the face-centered cubic structure of palladium (see Figure S2 in Supporting Information). Only reflection peaks from palladium were recorded. The (111) peak is sharper and much higher in intensity than the other peaks. Similar XRD patterns have been recorded for long Au nanorods.^{12b} Close examination of individual nanorods was performed by a TEM analysis. Figure 2a presents a TEM image of a Pd nanorod with a length of ~ 365 nm. It has a penta-twinned crystal structure that is typically observed for Au nanorods prepared by a seed-mediated growth process.^{12,20} Its selected-area electron diffraction (SAED) pattern, shown in Figure 2b, is also consistent with that reported for the penta-twinned Au nanorods and corresponds to a superposition of square [001] and rectangular [1 $\bar{1}$ 2] zone patterns of a face-centered cubic structure.²⁰ Thus, the Pd nanorods synthesized have a penta-twinned structure with five {111} facets at each end and five {100} side faces. The nanorod was grown along the [110] direction. High-resolution TEM image of an edge portion of this nanorod revealed clear lattice fringes with a measured d spacing of 2.28 Å, which should correspond to the (111) lattice planes. This result is consistent with the previous analysis on Au nanorods.^{12a,20} The pentagonal twinned structure of the nanorods can also be observed from their SEM images (see Figure 2d). The TEM image shown in Figure 2a reveals that the side faces of the nanorod are not all very flat. High-resolution TEM images indicate that this coating-like material is also palladium, as seen in Figure 2c. This surface feature may be related to the two-stage growth process used to make the Pd nanorods.

By simply increasing the volume of $\text{Cu}(\text{OAc})_2$ solution added to 250 μL , extensively branched Pd nanocrystals were synthe-

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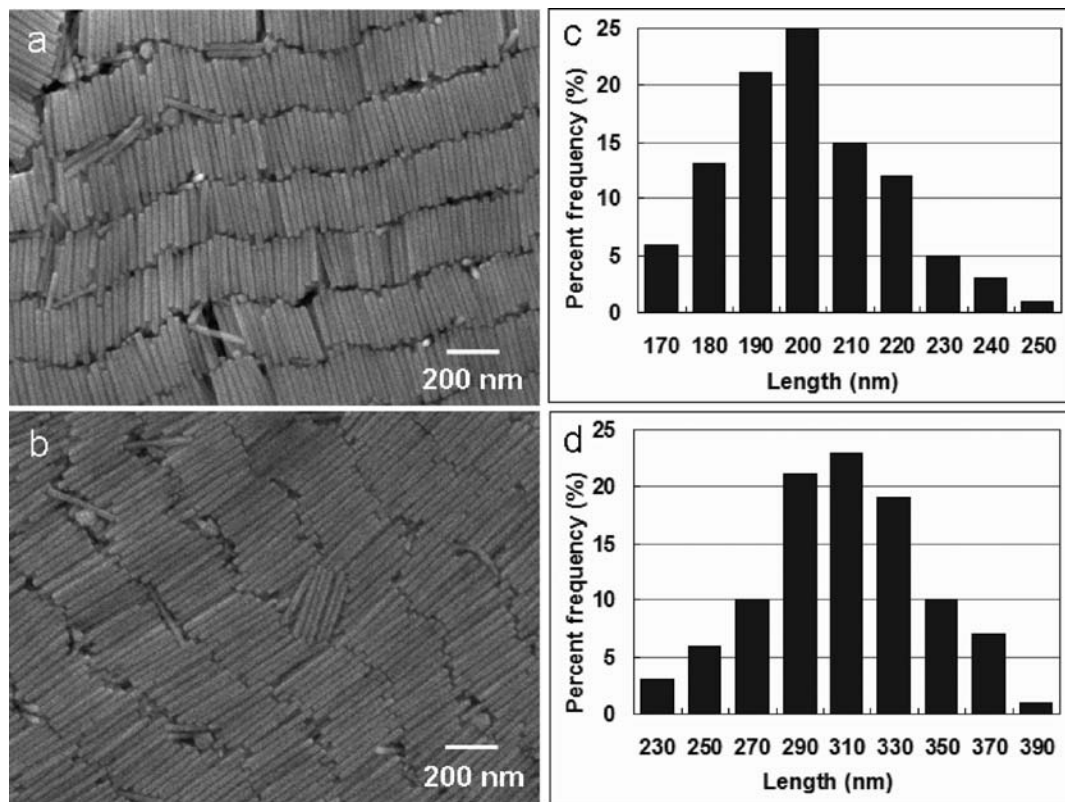


Figure 1. SEM images of the Pd nanorods synthesized by a seeding growth approach with the addition of (a) 50 μL and (b) 100 μL of 0.004 M $\text{Cu}(\text{OAc})_2$ into the growth solution in vial B. (c,d) Respective length distribution plots for samples a and b. The synthesized Pd nanorods precipitated to the bottom of the vial and can be obtained with a high yield of >95%.

Table 1. Average Lengths and Standard Deviations of the Lengths of the Palladium Nanorods Synthesized in Samples a and b

sample	amount of 0.004 M $\text{Cu}(\text{OAc})_2$ added	length (nm)	standard deviation (%)
a	50 μL	200 ± 17	8.5
b	100 μL	308 ± 34	11.0

sized. Figure 3 displays SEM images of the branched particles. Their XRD pattern is almost identical to that for the Pd rods (see Figure S2 in Supporting Information). For most of these particles, many branches were developed to give them a star shape. This type of branched particles presumably is derived from the overgrowth of the initially formed faceted particles. Pd nanostructures with this unique morphology are rarely seen. There is a second type of the branched nanoparticles with few arms, as highlighted in Figure 3c. These particles are produced through an overgrowth of the rods to form side arms or faceted particles to form tripods and tetrapods. Figure 4 gives the TEM images of the branched Pd nanocrystals with morphologies corresponding to those of particles 1 and 2 shown in Figure 3. For these nanocrystals, we focused our analysis on the branches. The side arms are single crystalline, and they do not possess a penta-twinned structure as seen in the nanorods. For particle 1, both the SAED pattern and high-resolution TEM image indicate that the branch grows along the [100] direction. For particle 2, the branch is also single crystalline. The SAED and TEM data suggest that this branch grows along the [111] direction. Thus, the branched nanocrystals can grow along different directions and should have mixed surface facets. Interestingly, both growth directions differ from that of the nanorods.

The growth mechanism for the formation of these Pd nanorods and branched nanocrystals was investigated in great

detail. The Pd seed particles have a diameter of ~ 3 nm (see Figure S3 in Supporting Information). After growth for 2 h in vial A, a mixture of spherical particles and short nanorods was generated. The particles have an average diameter of ~ 20 nm, while the nanorods have an average length of just ~ 40 nm (see Figure S4 in Supporting Information). To significantly increase the nanorod length, the short rods can serve as seed particles in the second growth stage with the addition of a small amount of copper acetate solution. Various volumes of the $\text{Cu}(\text{OAc})_2$ solution have been used, and the complete results are presented in Figure 5 to illustrate the overall growth process in the formation of long Pd nanorods and branched nanocrystals. The same products imaged over larger areas are also provided in Figure S5 in Supporting Information to see the full lengths of the nanorods. Without the introduction of Cu^{2+} ions, rods with lengths of 130–160 nm were produced along with the formation of faceted particles about 70 nm in diameter. The diameters of the short rods are 30–40 nm. Thus, aspect ratios of these rods are just 4–5. Addition of 50–100 μL of the $\text{Cu}(\text{OAc})_2$ solution led to a significant elongation of the nanorods with reduced diameters. The faceted particles have similar sizes as before, but they have a slightly distorted appearance. By further increasing the volume of the $\text{Cu}(\text{OAc})_2$ solution added from 150 to 300 μL , the faceted particles became highly distorted and then evolved into a star-like structure with multiple branches. The long nanorods have also developed branches at their two ends, and the side faces became roughened. The branched nanocrystals synthesized with the addition of 250 μL of the $\text{Cu}(\text{OAc})_2$ solution were examined in great detail in this study. Thus, Figure 5 clearly shows that, by fine-tuning the amount of $\text{Cu}(\text{OAc})_2$ added during particle growth, long Pd

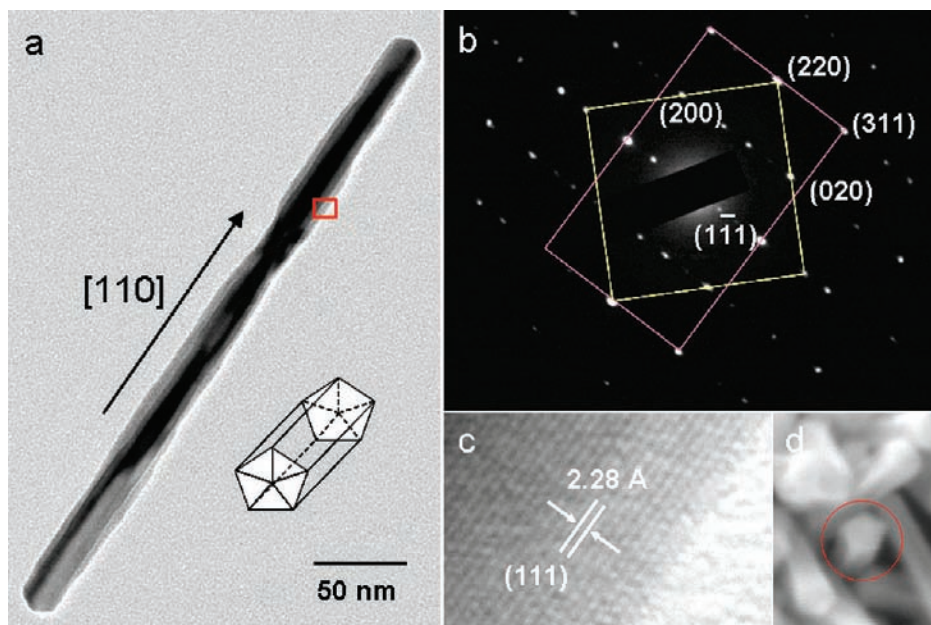


Figure 2. (a) TEM image of a Pd nanorod and a model of its five-fold-twinned structure. (b) SAED pattern of the Pd nanorod shown in panel a. The pattern indicates that the nanorod is grown along the [110] direction and corresponds to a superposition of square [001] (marked in yellow) and rectangular [112] (marked in purple) zone patterns of a face-centered cubic structure. (c) High-resolution TEM image of the square region in panel a. The measured d spacing of 2.28 Å corresponds to the (111) lattice planes of palladium. (d) SEM image of Pd nanorods showing a pentagonal twinned structure.

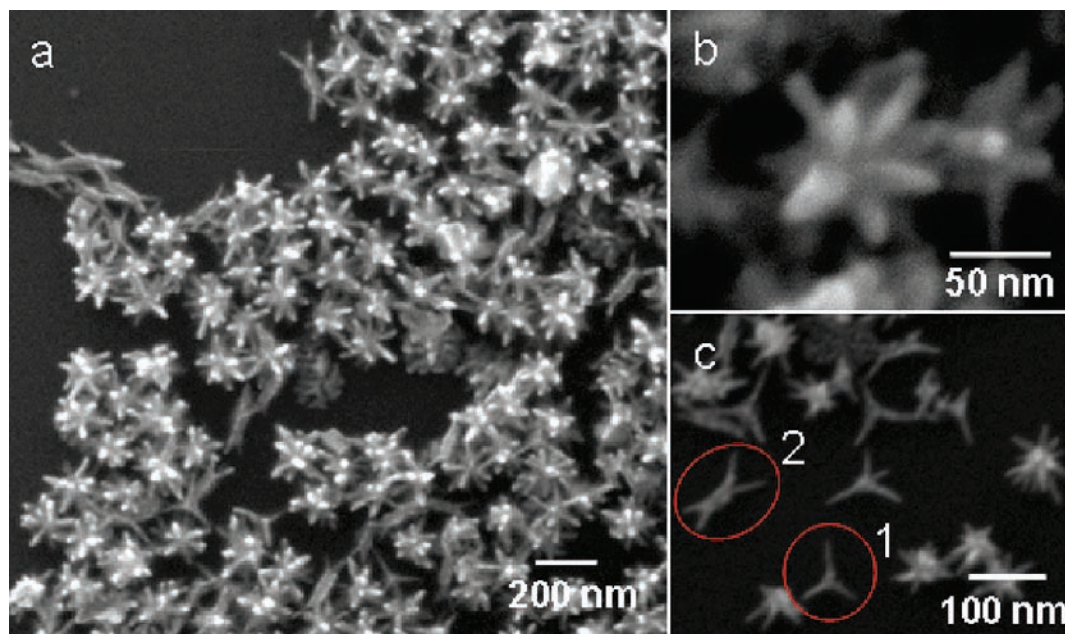


Figure 3. SEM images of the branched Pd nanocrystals. (a,b) Pd multipods shown at different magnifications. (c) Branched Pd nanocrystals with a somewhat different morphology. The star-shaped Pd nanocrystals were grown from faceted particles, while the elongated branched particles with few arms were derived from short rods. Branched particles labeled 1 and 2 are derived from a faceted particle and a short rod, respectively.

nanorods and extensively branched Pd nanocrystals can be selectively synthesized.

When the same volumes of the $\text{Cu}(\text{OAc})_2$ solution (i.e., 100 and 250 μL) was replaced with $\text{Ni}(\text{OAc})_2$, $\text{Zn}(\text{OAc})_2$, or AgNO_3 solution of the same concentration, long nanorods and branched nanocrystals were not produced. For both the $\text{Ni}(\text{OAc})_2$ and $\text{Zn}(\text{OAc})_2$ solutions, only faceted particles and short rods with similar lengths as those prepared in the absence of $\text{Cu}(\text{OAc})_2$ were formed (see Figure S6 in Supporting Information). No rods were observed with the addition of AgNO_3 solution at both volumes, but only faceted particles with smaller sizes than those

found in the other cases were generated. The results demonstrate that only $\text{Cu}(\text{OAc})_2$ is effective at forming long Pd nanorods and branched nanocrystals. To see if the acetate species is necessary for forming these Pd nanostructures, the same amounts of the $\text{Cu}(\text{OAc})_2$ solution were replaced with $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , and CuCl_2 solutions. All these copper ion sources produced the same long Pd nanorods and branched nanocrystals in high yields at the same corresponding volumes, revealing that the choice of the anion is not crucial (see Figure S7 in Supporting Information). The reason copper ions are effective at producing the long Pd nanorods is likely because copper has a somewhat

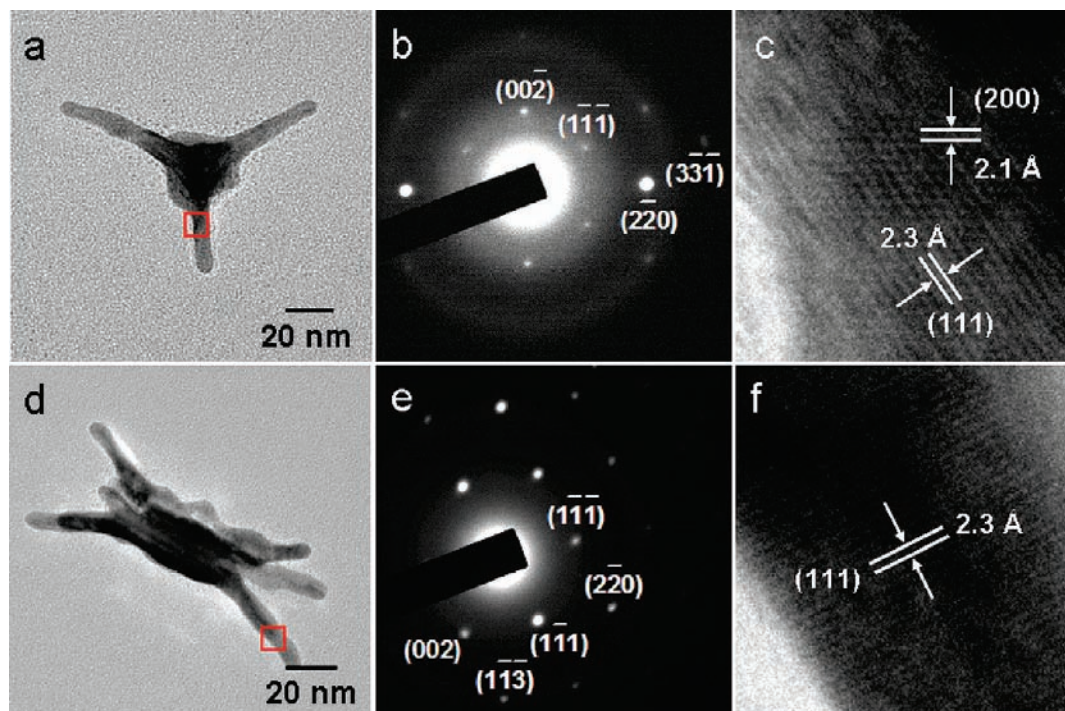


Figure 4. (a,d) TEM images of the branched Pd nanocrystals with morphologies corresponding to those of particles 1 and 2 shown in Figure 3. (b) SAED pattern of the square region in panel a. (c) High-resolution TEM image of the square region in panel a. The measured d spacings of ~ 2.3 and 2.1 Å correspond to the (111) and (200) lattice planes of Pd, respectively. The arm was grown along the [100] direction. (e) SAED pattern of the square region in panel d. (f) High-resolution TEM image of the square region in panel d. The measured d spacing of ~ 2.3 Å corresponds to the (111) lattice planes of Pd. The arm was grown along the [111] direction.

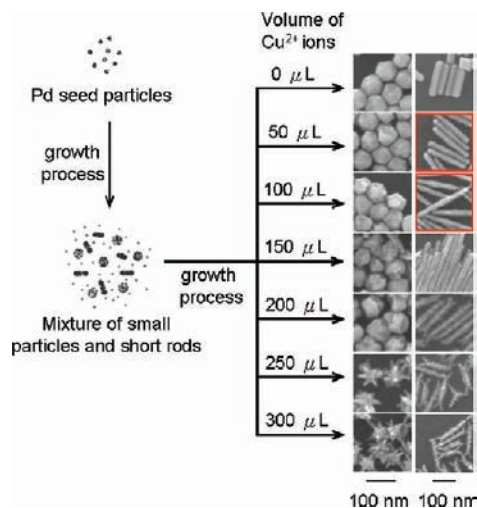


Figure 5. Growth process of the palladium nanocrystals and the final products obtained with the addition of different amounts of Cu^{2+} ions. The nanorods examined in this study are highlighted by the red squares.

smaller reduction potential (0.34 V for the half-reaction $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$) than that of palladium (0.60 – 0.623 V for the half-reaction $\text{PdCl}_4^{2-} + 2\text{e}^- \rightarrow \text{Pd} + 4\text{Cl}^-$).²¹ Because of their relatively close reduction potential values, some copper ions may be reduced and reoxidized at varying instants during the second growth stage and serve as deposition or nucleation sites on the preformed short Pd rods and faceted particles for their further growth into long rods and branches. At lower concentrations of copper ions, copper atoms may preferentially deposit

at or near the ends of rods because these regions are more accessible than the side faces of the rods capped by surfactant molecules and assist the one-dimensional growth into long nanorods.^{11,22} As higher amounts of copper ions are introduced, multiple deposition/nucleation sites can occur, leading to the formation of extensively branched particles. EDS mapping of long Pd nanorods showed low concentrations of copper atoms at various spots along the lengths of the rods, suggesting that their effect on the directed nanorod growth was persistent (see Figure S8 in Supporting Information). For metal ions with negative reduction potentials such as Ni^{2+} and Zn^{2+} ions, they simply stay in the solution and play no part in the synthesis process. Silver, having a larger reduction potential than that of palladium at 0.80 V, can significantly alter the morphology of the initially formed Pd nanoparticles such that even short rods disappear. From this reduction potential consideration, another example of this type of growth process is the formation of pentabranched Au nanocrystals derived from the side growth of pentagonal bipyramids with the introduction of a tiny amount of AgNO_3 .²³

Optical properties of these Pd nanostructures have been examined by taking their UV–vis absorption spectra (see Figure 6). The nanorods exhibit two absorption bands, which may correspond to the longitudinal and transverse surface plasmon resonance absorption bands observed for Au nanorods.¹² Because the longitudinal absorption mode appears in the near-infrared (near-IR) region, dried nanorod samples were used for the spectral measurements in this region. Both nanorod samples display a strong absorption band with its maximum below 250 nm. It is not clear if the shoulder band at ~ 250 nm, as seen

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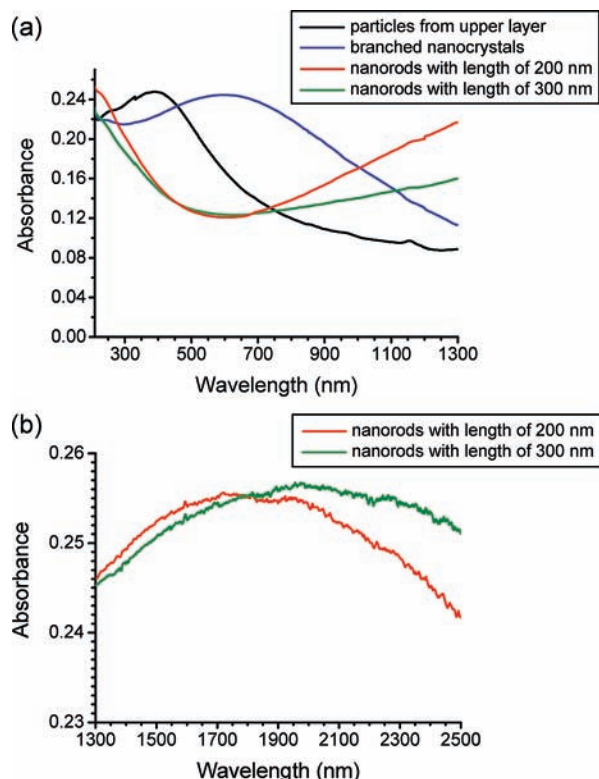


Figure 6. (a) UV-vis absorption spectra of the palladium nanoparticles from the upper layer, branched nanocrystals, and nanorods with average lengths of 200 and 308 nm. (b) UV-vis absorption spectra of palladium nanorods with average lengths of 200 and 308 nm in the near-IR region. A drop of the nanorod solution was added to the inside wall of a quartz cuvette and left to dry before the spectral measurements. Absorbance in panel a cannot be compared with that in panel b.

from the absorption spectrum of the faceted particles collected from the upper layer solution, is due to the absorption from the rods. The faceted particles show a broad absorption band at ~ 400 nm. The fact that this band is absent in the UV-vis spectra of the nanorod samples further demonstrates the efficient separation of the rods from the faceted particles. The longitudinal absorption band of the Pd nanorods with an average length of 200 nm shows a maximum at ~ 1800 nm, while that of the nanorods with an average length of ~ 300 nm is at 2000–2100 nm. Previously, a mixture of Pd nanocubes and short rods gave a UV-vis spectrum with continuous absorption across the full spectrum over a range of 200–700 nm.⁹ The UV-vis spectrum of the branched nanocrystals looks quite different from that of the long nanorods with a broad absorption band centered at around 600 nm.

Since Pd nanostructures of this large size are rarely considered for their applications in catalysis, we have examined the use of these Pd nanorods with an average length of ~ 300 nm and branched nanocrystals for catalyzing a Suzuki coupling reaction between phenylboronic acid and iodobenzene. To make sure that the nanostructures can maintain their structural integrity, they were first refluxed in the same EtOH/water solvent mixture as that used for the Suzuki coupling reaction for 1–3 h (see Figure S9 in Supporting Information). No change in the morphology of the Pd nanostructures was observed, suggesting that they are stable under the reflux condition. Then the Pd nanorods and branched nanocrystals were tested for their catalytic activity. The reaction conditions used and experimental results are shown in Table 2. Remarkably, high product yields

Table 2. Recyclability of the Pd Catalysts in the Suzuki Cross-Coupling Reaction

entry	catalyst	yield (%)
1	Pd nanorods	92
2	first recycle	89
3	second recycle	85
1	branched Pd nanocrystals	90
2	first recycle	86
3	second recycle	82

of 90–92% can be achieved using both Pd nanostructures. Turnover frequency (TOF) for the nanorods was calculated to be 14.4. A TOF value of 12.5 was determined for the branched nanocrystals. The same catalysts were used for the second and third cycle after adding fresh reagents. High product yields of 82–85% were still obtained after the third cycle of the Suzuki coupling reaction. The results demonstrate that the long Pd nanorods and branched nanocrystals can also serve as highly efficient and recyclable catalysts, with the consideration of their relatively large sizes. The morphologies of the Pd nanostructures after the first and second cycle of reaction were examined, and again no change was found (see Figure S10 in Supporting Information). The slight decrease in the percent yields for the second and third cycle may be due to their partial aggregation and/or the loss of some particles adhering to the wall of the flask. Better experimental design and the use of a longer reaction time should improve the percent yields. It is worthy to note that the mol % of Pd catalysts used here is less than that employed in the study using hollow Pd spheres as catalysts (3 mol %).¹⁸ These Pd nanostructures can also be easily removed from the product solution, so the solution is free from catalyst contamination. It is expected that these nanorods and branched nanocrystals should catalyze other types of reactions.

Conclusion

We have successfully used a seed-mediated synthesis approach to prepare uniform palladium nanorods with average lengths of ~ 200 and 300 nm. The addition of a small amount of copper acetate solution during the nanorod growth stage was found to be the key to the generation of long Pd nanorods. Because of their long lengths, they settled as a precipitate to the bottom of the reaction vial and can be easily separated from the suspended faceted particles in the solution. By slightly increasing the volume of the copper acetate solution introduced, extensively branched Pd nanocrystals were synthesized. The crystal structures of both particle morphologies were carefully examined. The role of copper ion source was investigated. A close but lower reduction potential of copper relative to that of palladium leads to periodic deposition and reoxidation of copper atoms on the Pd nanorods and faceted particles, and this facilitates their growth into long rods and branches. UV-vis spectra of these Pd nanorods showed a significant absorption band in the near-IR region with peak maxima in the range of 1800–2100 nm. Both the long Pd nanorods and branched nanocrystals have been demonstrated to serve as highly efficient and recyclable catalysts for catalyzing a Suzuki coupling reaction. They are also thermally stable under the reflux condition and can be easily removed from the product solution. With these advantages, these novel Pd nanostructures are expected to find use in many other types of palladium-catalyzed reactions.

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Supporting Information Available: SEM images of the Pd nanorods and branched nanocrystals over large areas, XRD patterns, TEM images of the seed particles and short nanorods, SEM images of the products formed using different volumes

of $\text{Cu}(\text{OAc})_2$ solution, SEM images showing the effects of using different copper ion sources and anions, EDS mapping of the Pd nanorods, and SEM images of the Pd nanorods and branched nanocrystals after the reflux procedure and the Suzuki coupling reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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