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Facile Approach to Prepare Pd Nanoarray Catalysts within Porous Alumina Templates on Macroscopic Scales

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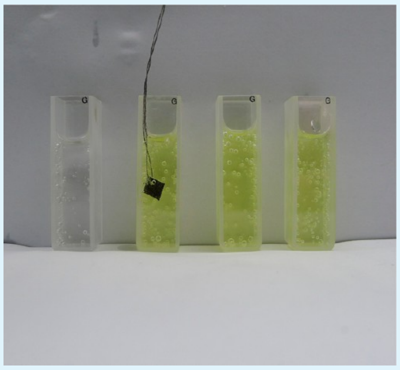
Supporting Information

ABSTRACT: The separation and reuse of nanocatalysts remains a major challenge. Herein, we report a novel approach to prepare palladium nanowire array catalysts by reducting $PdCl_2$ in the pores of anodic aluminum oxide (AAO) templates with backside Al sheets via a hydrothermal process. Suzuki coupling reactions and 4-nitrophenol (4-NP) reduction reactions were employed to study the catalytic activity of the nanocatalysts. The nanocatalysts demonstrated good activity, great thermal stability, easy separation, and excellent reusability in both Suzuki reaction and 4-NP reduction.



KEYWORDS: *AAO, Pd, heterogeneous catalysts, nanoarray, Suzuki reaction, high temperature stability*

INTRODUCTION

Noble-metal nanostructures with varied size, shape, and composition are potentially useful in many fields such as SERS,[1] biological sensing,[2] imaging,[3] medical diagnostics,[4] cancer therapy,[5] optics,[6] and catalysis.[7,8] In the field of catalysis, heterogeneous catalysts are favored over homogeneous ones because of their superior features, such as their simplicity in recovery and regeneration.[9] Nanoparticles have emerged as an attractive alternative compared to conventional catalysts because of their many advantages such as larger surface-to-volume ratio and greater activity, selectivity, and stability.[10] However, two major problems prevent their large-scale application. First, the isolation and recovery of tiny nanocatalysts from the reaction mixture are not easy. Second, the activity of the nanocatalysts is usually reduced because of agglomeration and leaching.[11] Attempts have been made to address these issues by immobilizing the active species on nanometer-sized solid supports with high surface area such as metal oxide,[12] silica,[13] carbon,[14] polymer,[15] nanocomposites,[16,17] and magnetic nanoparticles.[18] However, the recovery of these supported nanocatalysts is limited to a certain extent because of the nanoscale of the supports.[19,20]

Furthermore, ordered porous solids materials of micrometer size such as MgO,[21] KF/Al_2O_3,[22] Al_2O_3,[23] MgLa,[24] and LDH (double-layered hydroxide)[25] have been tested as the supports. Gniewek et al. reported the preparation of lumina-based oxides (Al_2O_3, Al_2O_3−ZrO_2, and Al_2O_3−ZrO_2−Eu_2O_3) by a sol−gel method and used them as supports for palladium nanoparticles.[26] Other ordered mesoporous materials, such as porous silicon,[27] zeolite,[28] and anodic aluminum oxide,[29] have also been used as supports for nanocatalysts. Although these mesoporous materials can be separated by filtration or centrifugation, complete removal and recycling can hardly be achieved, which greatly limits their application in chemical industries where metal contamination is highly regulated, such as in the pharmaceutical industry. These materials also share severe limitations related to the strength of acid sites and thermal/hydrothermal stability because of the amorphous nature of the mesostructured materials.[30] Another key challenge is the leaching and aggregation of the nanocatalysts, leading to a reduction in the activity after several cycles.[21,22] For example, using mercaptopropyl or aminopropyl ligands, Pd nanocatalysts supported on functionalized silica was slowly deactivated after three runs in Suzuki coupling reactions.[31]

Materials on the macroscopic scale such as oxide, activated carbon, and organic or hybrid polymer resin[32] have been widely used as supports for nanocatalysts. These materials have the advantage of being easily separated from the reaction mixture and reused. However, the low surface-to-volume ratio and leaching problems have greatly limited their use. Employing noble nanorods or nanowires with high activity instead of nanoparticles is another choice for a nanocatalyst.[33] Herein, we

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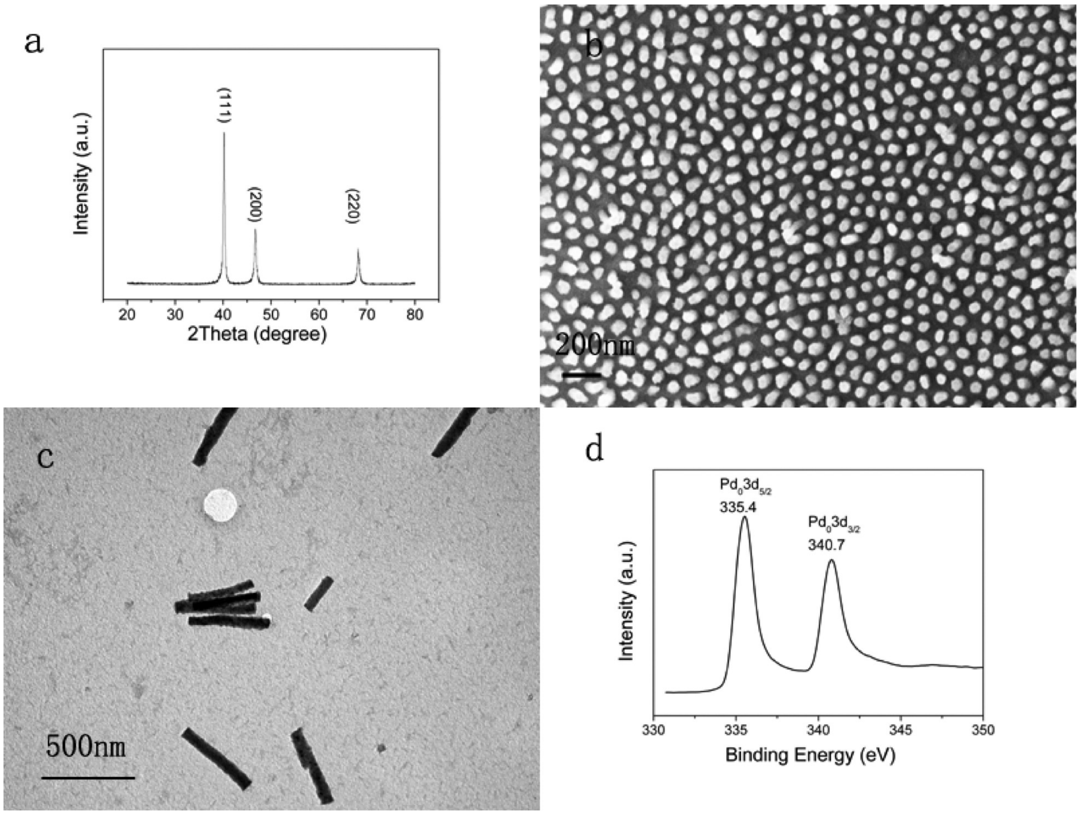

Figure 1. (a) XRD patterns of Pd nanowires collected after dissolving AAO templates. (b) SEM image of Pd nanowires array grown in the pores of AAO. (c) Representative TEM image of typical Pd nanowires formed in the hole of AAO. (d) XPS spectrum of Pd 3d in Pd nanowires.

report a simple way to prepare macroscopic-scale catalysts with palladium nanowire confined in the pores of anodized aluminum oxide (AAO) templates on backside Al sheets through a technique recently developed by our group.[34] The synthesis of AAO is simple, low-cost, and scalable, and the templates can easily achieve excellent long-range order.[35] Additionally, the nanoarrays are confined in the AAO template and were not easily agglomerated. The AAO-supported palladium catalysts showed great activity, stability, and reusability in the Suzuki coupling and 4-NP reduction reactions. These results demonstrate an easy approach to simultaneously address the decreased stability and reusability issues commonly encountered in nanocatalysts.

■ RESULTS AND DISCUSSION

After dissolving the AAO templates and Al substrates in a 3.0 M NaOH aqueous solution, the palladium nanowires were characterized by X-ray (Cu Kα) powder diffraction (XRD). As shown in Figure 1a, all reflection peaks can be indexed to face-centered cubic Pd. The crystalline size is calculated to be 40 nm from the (111) peak according to Scherrer's equation. The field-emission scanning election microscopy (FESEM) image reveals that Pd nanowires grow within the pores of AAO to produce a 2D Pd array (Figure 1b). The nanowires vary in size from 50 to 70 nm in diameter. Nanowires with a size of less than 40 nm in diameter can also be synthesized (Figure S1) A representative TEM image of the Pd nanowires obtained by wet etching of an AAO template is shown in Figure 1c. It was confirmed that the length of the nanowires was around 500 nm, which conforms to the results from the calculation of the weight. The X-ray photoelectron spectroscopy (XPS) spectrum of Pd 3d can be fitted into a main doublet peak (Figure 1d). The binding energy of the doublet peaks at 335.4 (assigned to Pd03d$_{5/2}$) and 340.7 eV (assigned to Pd03d$_{3/2}$) can be attributed to the Pd(0) state. These results indicate that the Pd species within the pores of AAO template was elementary Pd(0) without the presence of any PdO. The growth mechanism of the Pd nanowires in the pores of AAO is attributed to electron transfer from the Al plate to Pd^{2+} ions according to the principle related to battery technology (Al(s) | AlCl$_3$(a1) | PdCl$_2$(a2) | Pd(s)), which is also similar to the deposition of Ni nanowires in the pores of AAO (Figure S2).[34]

To evaluate the catalytic ability of the AAO-supported Pd nanowires, Suzuki cross-coupling reactions were carried out as a model reaction. The Suzuki cross-coupling reaction of arylhalides and phenylboronic acid provides an efficient route to form C−C bonds under relatively mild conditions.[36] The reactions were conducted using ethanol as the solvent and K$_2$CO$_3$ as the base. To ensure the nanowires were exposed, a 1 mol/L NaOH solution was used to dissolve the surface layer of the AAO template. As shown in Table 1, iodobenzene and bromobenzene showed good results because of their high reactivity (Table 1, entries 1 and 2). 4-Bromotoluene was used instead of bromobenzene to confirm that the biphenyl was cross coupled by arylhalides and phenylboronic acid rather than by self-coupling of phenylboronic (Table 1, entry 3). The result shows that the yield of 4-phenyltoluene was upwards of 78% with very little biphenyl generated. The kinetic profiles of the three reactions (Table 1, entries 1, 2, and 3) were obtained on the basis of the GC results (Figure S3). In addition, the mass balance on the basis of the GC results indicated no side reaction. Pure AAO template on Al sheets was not able to catalyze the reaction (Table 1, entry 4).

Table 1. Suzuki Reactions Catalyzed by the AAO Supported Pd Nanowires Catalysts[a]

entry	R1	X	T (°C)	yield (%)[b]	TOF[c]
1	H	I	60	96	48.2
2	H	Br	60	90	45.2
3	CH_3	Br	60	78	39.1
4[d]	H	I	60	0.8	N/A
5[e]	CH_3	Br	150	92	46.2
6	H	Cl	60	25	12.6
7[e]	H	Cl	150	84	42.2

[a]Reaction conditions: a piece of Al sheet with Pd nanowires catalyst (1.2 cm diameter), 1 mmol arylhalide, 1.2 mmol phenylboronic acid, 3 mmol K_2CO_3, EtOH 30 mL, 2 h. [b]Isolated yield. [c]TOF is defined as mol product, mol^{-1} Pd h^{-1}. [d]Pure AAO template on an Al sheet was used. [e]Using DMF instead of EtOH.

The separation, stability, reusability, and leaching of catalysts are crucial for practical applications. (i) In our system, the catalysts can be easily separated/recovered simply by taking them away from the solution with tweezers. (ii) This catalyst demonstrated great thermal stability with high activity at elevated temperatures (Table 1, entry 5). The SEM image (Figure S4a) of the catalyst after reaction at 150 °C indicated that the surface morphology of nanoarrays was not changed. As for chlorobenzene and 4-chlorotoluene (Table 1, entries 6 and 7), the effect of substituted groups in the substrates was also investigated and shows that the conversion of substituted substrates is lower than of unsubstituted ones. Fortunately, most of the reactions can result in satisfactory yields by increasing the reaction temperature and changing the solvent or reaction time. The XPS spectrum (Figure S4b) of the catalyst after high-temperature reaction indicated that no oxidation took place. (iii) The AAO-supported Pd nanowires can be reused five times with no obvious decrease in their conversion rate and selectivity (Table 2; the three reactions studied are from Table 1, entries 1, 2, and 5). The reusability capability of the catalyst is maintained at 150 °C. Moreover, the kinetic studies of five cycles showed that the initial and subsequent rates of each cycle were not reduced (Figure 2). (iv) Finally, leaching of the catalysts into the reaction mixture was not observed. The Pd content in the filtrate after the first reaction as well as after five cycles was determined to be lower than 33 ppb by ICP-AES, indicating <0.1% Pd loss even after five cycles (Table 2). The results suggest that Pd element loss was due to element leaching in the Suzuki reaction[37] rather than the drooping of the Pd nanowires.

Table 2. Catalytic Performance of Pd Nanowires Catalysts Reused Five Times in Successive Suzuki Reactions

entry[a]	1	2	3	4	5	Pd loss (%)
1	96	97	96	94	95	<0.1
2	90	89	86	87	88	<0.1
5	92	91	89	87	88	<0.1

[a]The entry number corresponds to entries in Table 1.

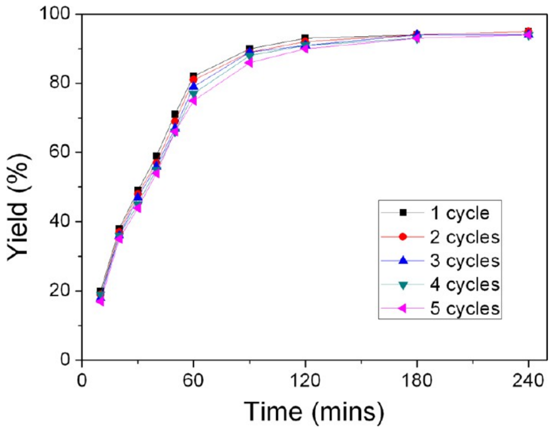

Figure 2. Kinetic profiles for five cycles of coupling reactions (the reaction conditions were similar to that for Table 1, entry 1).

The catalytic activity can be improved by using thinner Pd nanowires of 40 nm in diameter (Table S1). The catalytic activity of our catalysts is comparable with other supported nanocatalysts (Table S2). Most of the previously reported supported nanocatalysts were used at relatively low temperatures in Suzuki coupling reactions to avoid agglomeration and leaching. In contrast, the AAO-supported Pd nanowires demonstrated great thermal stability. Although our catalyst needs to be used in a greater amount than other supported nanocatalysts, this catalyst system possesses superior features such as easy separation, great reusability, high temperature stability, and minimum metal loss and serves as a promising candidate in many industrial applications.

The reduction of 4-NP by $NaBH_4$ in aqueous solution by the AAO-supported Pd nanowires was also tested.[38] The UV−vis absorption spectrum of an aqueous mixture of 4-NP and $NaBH_4$ has an absorption maximum at 400 nm because of the 4-NP ion in alkaline conditions. Without catalyst, the reduction cannot proceed, the maximum absorption peak remains unaltered, and the mixture maintains a yellow color. However, when a 3×3 mm^2 piece of Al sheet with Pd nanowire catalysts was added, the reaction is completed in 7 min. Time-dependent UV−vis absorption spectra show the decrease of the absorption peak at 400 nm and the concomitant development of a new peak at 300 nm corresponding to 4-aminophenol (4-AP), which is the reduction product of 4-NP (Figure 3a). The concentration of $NaBH_4$ is much higher than that of 4-NP and remains approximately constant during the reaction. Pseudo-first-order kinetics was observed with respect to 4-NP. The rate constant, k, was determined to be 6.5×10^{-3} s^{-1} from the plot of $\ln(A_t/A_0)$ (A is the absorbance at 400 nm) versus reduction time (Figure 3a, inset). The Pd nanowires at 40 nm in diameter gave a faster rate constant of 8.3×10^{-3} s^{-1} (Figures S5). This is consistent with the above results showing that thinner Pd nanowires gave higher reaction activity. The activity in this catalyst system is comparable with other reported catalysts (Table S3).

This catalyst system has great reusability and displayed ca. 94% activity after eight cycles (Figure 3b). Moreover, the reusability and ease of separation can be clearly demonstrated visually (Figure 4). First, 0.1 mL of 4-NP (0.003M) and 0.1 mL of $NaBH_4$ (0.3 M) were added in an orderly fashion into four quartz cuvettes containing 3 mL of distilled water, and a piece

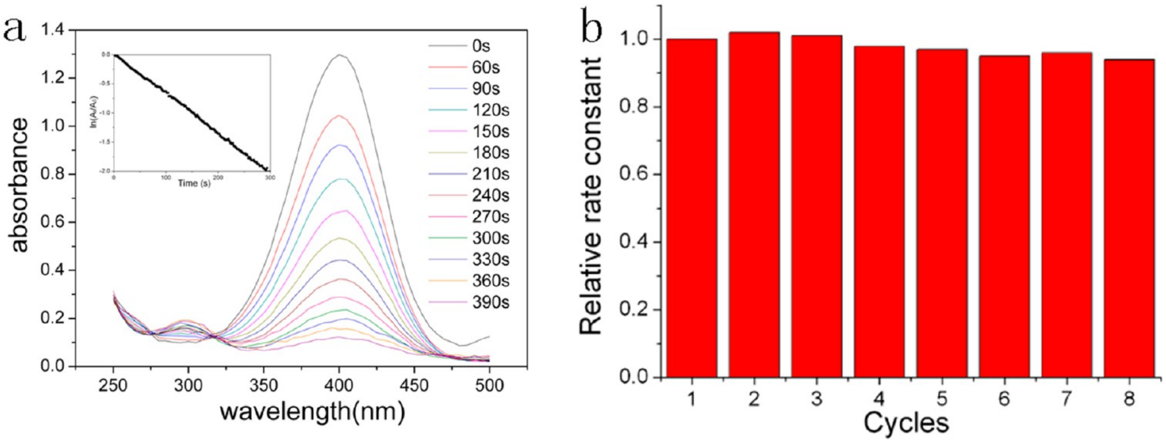

Figure 3. Catalytic reduction of 4-NP to 4-AP. (a) Time-dependent absorption spectra of the reaction solution in the presence of the Al sheet with 60 nm Pd nanowire catalysts (3×3 mm^2). The inset is the plot of $\ln(A_t/A_0)$ against reaction time. (b) Normalized rate constant for different cycles of the reduction of 4-NP to 4-AP.

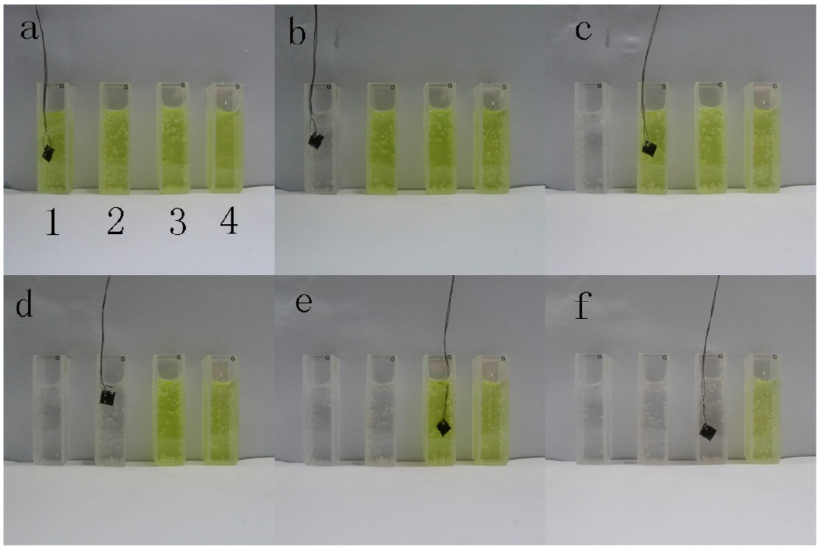

Figure 4. Photographs of recycled 4-nitrophenol reduction. (a) Beginning of the reaction in cuvette 1. (b) End of the reaction in cuvette 1. (c) Beginning of the reaction in cuvette 2. (d) End of the reaction in cuvette 2. (e) Beginning of the reaction in cuvette 3. (f) End of the reaction in cuvette 4. Cuvette 4 is the control sample.

of Al sheet with Pd nanocatalysts was put into cuvette 1 (Figure 4a). After about 5 min, the 4-NP in cuvette 1 was reduced to 4-AP, and the color of the solution in cuvette 1 was changed from yellow to colorless (Figure 4b). Second, the nanocatalysts were taken away from cuvette 1 and put into cuvette 2 (Figure 4c). Similarly, the solution in cuvette 2 became transparent after 5 min (Figure 4d). Last, the nanocatalysts were taken away from cuvette 2 and put into cuvette 3 (Figure 4e). Again, the color of the solution in cuvette 3 disappeared in 5 min (Figure 4f). Cuvette 4 is the control sample. The solution did not contain any Pd after the reaction on the basis of ICP-AES analysis.

The unique growth mechanism of the Pd nanowires enables their strong affinity to the AAO templates. The backside Al sheets of the AAO membrane not only reduces the Pd^{2+} ions to Pd metal nanowires but also acts as a substrate to support the Pd nanowires, which makes the separation of the catalyst from the reaction mixture very easy. The diameter of the nanopores can be easily controlled from 20 to 200 nm by controlling the pore size of the AAO templates. As shown earlier, the diameter of the Pd nanowires is crucial to the catalytic activity. This technique to prepare AAO-supported noble-metal nanowire catalysts has many advantages: (1) a large variety of metal nanowires can be prepared as long as their electrode potential is greater than that of aluminum; (2) the system is simple to set up, easy to operate, and durable for industrialization; (3) the catalysts synthesized this way can be easily separated from the reaction mixture and reused without an obvious reduction in activity, which is beneficial for commercial catalytic processes; (4) excellent catalysis performance and repeatability for the Suzuki cross-coupling and 4-nitrophenol reduction reactions owing to the high stability of the nanocatalysts, including the high affinity of the palladium nanowires and AAO template because of the unique growth mechanism and because of the isolated Pd nanowires separated by the AAO template frame.

■ CONCLUSIONS

We have reported a novel method to prepare Pd nanowires array in AAO templates with a backside Al sheet by direct chemical reduction of Pd^{2+} ions with the Al substrate of AAO. The catalyst exhibits good activities for various Suzuki coupling reactions and 4-nitrophenol reduction. Furthermore, the nanocatalysts supported on macroscopic-scale AAO could be easily separated and recycled and could be reused five times without a reduction in catalytic activity or Pd loss. This approach provides a simple, cost-effective, and scalable method to produce different noble- and transition-metal and alloy nanocatalysts.

EXPERIMENTAL SECTION

The detailed process for preparing Pd nanoarrays is schematically shown in Figure S2. The AAO template on the backside of Al sheets was synthesized as described in ref 32. In a typical procedure, the AAO template with aluminum substrates enveloped by a Teflon bracket was sealed in a 50 mL Teflon autoclave filled with $PdCl_2$ (1 mg) solution followed by hydrothermal treatment at 120 °C for 2 h and cooled to room temperature naturally. The AAO template with Pd nanowires was collected after washing with deionized water several times and subsequently dried in vacuum at 60 °C for 3 h.

In a typical Suzuki cross-coupling reaction, a piece of Al sheet with Pd nanowire catalysts (1.2 cm diameter; Table 1 indicates that about 0.53 mg of Pd was analyzed by ICP) was attached to a stirring rod with the stirring speed set at 300 r/min, and 1 mmol arylhalide, 1.2 mmol phenylboronic acid, and K_2CO_3 (3 mmol) were added to 30 mL of alcohol. The reactions were carried out under reflux conditions for 4 h. Then, the reaction mixture was analyzed by gas chromatography−mass spectrometry.

In a typical 4-NP reduction reaction, 0.1 mL of 4-NP (0.003 M) and 0.1 mL of $NaBH_4$ (0.3 M) were added into a quartz cuvette containing 3 mL of distilled water. A 3 × 3 mm^2 piece of Pd nanowires catalyst was put into the cuvette to start the reaction. The time-dependent UV−vis spectroscopy absorption spectra of the reaction mixture were recorded in a spectrophotometer. The progress of the reaction was monitored by the disappearance of the peak at λ_{max} = 400 nm, which corresponds to the 4-nitrophenolate ion.

ASSOCIATED CONTENT

Supporting Information

SEM of the Pd nanowires array of about 40 nm in diameter, mechanism and schematic diagram of the Pd nanowires growth process, Suzuki reactions catalyzed by 40 nm Pd nanowires catalysts, kinetic profiles for coupling reactions, SEM image and XPS spectrum of the Pd nanocatalyst after reaction at 150°C, catalytic performance of different Pd-based catalysts in the coupling reaction of bromobenzene and phenylbronic acid over the past 2 years, catalytic reduction rate of 4-NP to 4-AP with 40 nm Pd nanowires catalyst, and comparison of the pseudo-first-order rate constant for nitrophenol reduction by nanomaterials containing Pd nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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