

Facile synthesis of highly active Pd-Cu nanowires catalyst through a simple wet-chemical strategy for ligand-free Suzuki cross coupling reaction

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ABSTRACT

The construction and design of nanomaterials are important for improving their performance. Here we present a simple one-pot wet-chemical method for the preparation of alloyed Pd-Cu nanowires using octylphenoxypolyethoxyethanol (NP-40) as structure-directing and stabilizing agents. The obtained nanocrystals display outstanding catalytic activity for ligand-free Suzuki cross coupling reaction under mild conditions, and can be easily recovered and reused for at least 5 consecutive cycles without showing significant loss of catalytic activity.

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1. Introduction

Catalysis based on transition metal nanomaterials has emerged as a tremendously powerful synthetic tool in the development of industrial processes, especially in the production of fine chemicals [1,2]. Palladium (Pd) as an active transition metal has been extensively employed in organic catalysis [3]. In particular, the help of Pd-based catalyst, Suzuki cross-coupling reactions for the construction of C–C bonds successfully proceed under mild conditions [4]. However, common Pd catalysts suffer from high cost [5], hard to reuse due to difficulty in separation from the reaction mixture [6], as well as low effective atom utilization [7]. Pioneering studies revealed that a catalyst can boost its performance through the tuning of size, feature, and composition [8–11]. Transition metal nanoparticles (NPs) attracted considerable attention due to their enlarged surface-to-volume and multiple functionalities [12–14]. During the past decade, a number of nanocatalysts with various structures were prepared, such as cube [15], plate [16], star [17], rod [18], wire [19], chain [20], and other nanostructures [10]. Among

them, one-dimensional (1D) nanowires have attracted significant attention, owing to their unique architecture and pronounced catalytic performance [21–23].

Bimetallic catalysts show obvious advantages as compared to the monometal counterparts, such as enhanced catalytic activity, improved stability and selectivity derived from synergistic effects [24]. In recent years, great advances have been achieved in their preparation and practical catalytic applications [25,26]. Particularly, a larger amount of bimetallic Pd-based catalysts (PdM) were constructed, where M represents another transition metal such as Pt [27], Au [28], Ag [29], Ni [30], Co [31], and Cu [32]. Of the transition metals, Cu is well accepted as one of the most prominent, important, and promising catalysts because of its versatility, low cost and abundant reserve [33,34]. Thus, it is envisaged that a combined use of Pd and Cu can reduce the cost of Pd-based catalysts, and the combination of Pd with Cu can enhance the stability in the field of catalysis.

In this article, we report an efficient one-pot wet chemical strategy to fabricate the generation of Pd-Cu nanowires (denoted as Pd-Cu NWs) by using substitute octylphenoxypolyethoxyethanol (NP-40) as the structure-directing and stabilizing agent. The catalytic activity of the as-obtained Pd-Cu NWs was investigated by choosing the classical Suzuki cross-coupling reaction as model reaction.

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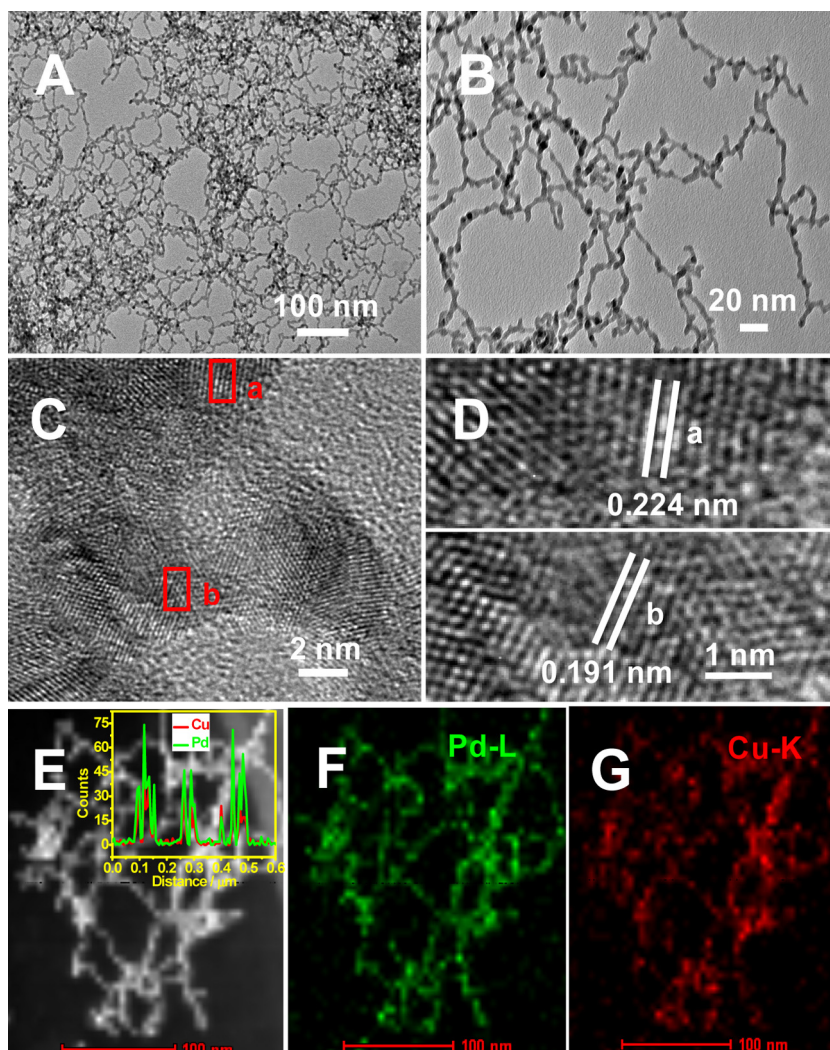


Fig. 1. Low (A), medium (B), and high magnification (C–D) TEM images of Pd-Cu NWs, along with the associated HAADF-STEM-EDS mapping images (E–G). Inset in (E) shows the corresponding line scanning profiles.

2. Experimental

2.1. Materials

The reagents employed in the experiments were of analytical grade and used as received: Palladium chloride (PdCl_2), cupric chloride (CuCl_2), substitute octylphenoxypolyethoxyethanol (NP-40, 10% in H_2O), sodium borohydride (NaBH_4) (98 wt%), penylboronic Acid (97 wt%), and commercial Pd black (99.9 wt%) were from Shanghai Aladdin Chemical Reagent Company (Shanghai, China). The H_2PdCl_4 (100 mM) solution was prepared by adding 0.4 mL concentrated hydrochloric acid to dissolve the PdCl_2 . And twice distilled water was used for the preparation of the aqueous solutions throughout the entire study.

2.2. Instrumentations

Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), X-ray energy dispersive spectroscopy (EDS), and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) were employed to characterize the morphology, composition, and metal distribution of the obtained nanocrystals, which were all performed over a JEM-2100F transmission electron microscope coupled with an energy dispersive

X-ray spectrometer with an accelerating voltage of 200 kV and applied Mo grid as the substrate. The crystal structures were determined by X-ray diffraction (XRD) spectroscopy (Bruker-D8-AXS diffractometer system, $\text{Cu K}\alpha$ radiation). X-ray photoelectron spectroscopy (XPS) measurements were conducted by using a thermofisher-ESCALAB 250 (ThermoFisher, $\text{Al K}\alpha$ X-ray radiation with 1486.6 eV for excitation).

^1H NMR and ^{13}C NMR spectra were employed to characterize the as-prepared organic compounds. ^1H NMR spectra were recorded on Bruker Avance 400 MHz spectrometer in CDCl_3 [Internal standard: CDCl_3 (for ^{13}C , $\delta = 77.00$)]. ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in CDCl_3 [Internal standard: CDCl_3 (for ^{13}C , $\delta = 77.00$)]. The relevant physical properties, ^1H NMR and ^{13}C NMR spectra and mass analysis data (obtained over USA Thermo Finnigan Corporation, MAT 95 XP) of the products were provided in the Electronic Supplementary Information (ESI).

2.3. Synthesis of Pd-Cu nanowires

To fabricate the Pd-Cu NWs, 1 mL of H_2PdCl_4 (100 mM) and 1 mL of CuCl_2 (100 mM) were dropped into a beaker containing 48 mL of NP-40 solution (0.2%, w/v) in the ice water bath under stirring. Then, 3 mL of freshly-prepared 0.1 M NaBH_4 solution was poured into the mixture all at once under stirring, making the color change

promptly into black. After 5 min, the black mixture was allowed to stand overnight without stirring. The resulting black precipitates were collected by centrifugation and washed with water and ethanol. The final products were dried in an oven (50 °C).

2.4. Catalytic performance for suzuki cross coupling reactions

In the Suzuki cross coupling reactions, a mixture of phenylboronic acid (0.6 mmol, 1.2 equiv), aryl halide (0.5 mmol, 1 equiv), K_2CO_3 (1 mmol, 2 equiv), and Pd-Cu NWs (4 mg) were placed in a Schlenk tube (10 mL), which contained 2 mL of *N,N*-dimethylformamide (DMF) and water (H_2O) (v/v = 1/1). The mixture was then stirred for a desired period of time at a selected temperature, and the reaction was monitored by thin layer chromatography (TLC). Afterward, the reaction mixture was cooled down to room temperature. And the catalyst was recovered by filtration, followed by washing thoroughly with ethyl acetate and water. The combined organic layer was dried by Na_2SO_4 , and the filtered residue was purified by flash column chromatography on silica gel. As for the recycling experiments, we conducted several parallel experiments under identical conditions and recycled the catalyst for next run test. The target reactions would get supplement of catalysts from the other parallel experiments to make sure the scale of catalyst with 4 mg.

3. Results and discussion

3.1. Characterization

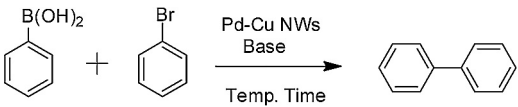
As shown in Fig. 1, we have successfully developed a facile and efficient synthetic procedure to fabricate Pd-Cu NWs. Fig. 1A–D are the typical TEM images of the product. From the low-magnification TEM image (Fig. 1A), one can see high-quality intertwining nanowires with average width of about 4 nm (Fig. 1B), and there is no detection of any nanoparticles throughout the entire image. As illustrated in the HR-TEM images (Fig. 1C–D), there is the confirmation of crystalline nature and display of well-resolved lattice fringes with adjacent spacings of 0.224 and 0.191 nm (marked), corresponding to the (111) and (200) planes of face-centered cubic (fcc) metal [32,35], respectively. Furthermore, the lattice spacing distances are between that of Pd (0.225 nm, 0.195 nm) and Cu (0.209 nm, 0.181 nm) single crystals, indicating the formation of Pd-Cu alloy [36].

In order to determine the distribution of Pd and Cu in Pd-Cu NWs, we collected the HAADF-STEM-EDS mapping images and EDS line scanning profiles (Fig. 1E–G). Noticeably, Pd and Cu are homogeneously distributed across the whole nanowires (Fig. 1E–G). Furthermore, the compositional line scanning profiles confirm their homogeneous distribution once again (Inset in Fig. 1E), providing another piece of evidence for the successful formation of Pd-Cu alloy.

The EDS spectrum in Fig. 2A further confirms the coexistence of Pd and Cu elements. And the atomic ratio of Pd to Cu in Pd-Cu NWs is roughly 1:1. The observations match well with the results of line scanning profiles (Inset in Fig. 1E), indicating the effective reduction of the Pd and Cu precursors. The XRD spectra of the as-prepared nanocrystals provide information related to composition and crystal structure (Fig. 2B). The (111) peak of Pd-Cu NWs shows up at 2θ (d-values) of 41.15° , which is between that of pure Pd (40.12°) and Cu (43.29°), further showing the formation of Pd-Cu alloy.

The XPS measurements were used to probe into the surface states of Pd-Cu NWs. It is observed that the $Pd\ 3d_{5/2}$ and $3d_{3/2}$ peaks are predominant in the high-resolution Pd 3d spectrum (Fig. 2C), revealing the efficient reduction of H_2PdCl_4 during syn-

Table 1
Optimization of the reaction conditions.^a

					
Entry	Solvents	Bases Temp.	Time (°C)	Time (h)	Yield (%) ^b
1	EtOH	K_2CO_3	80	2	40
2	CH_3CN	K_2CO_3	80	2	24
3	DMSO	K_2CO_3	80	2	62
4	DMF	K_2CO_3	80	2	76
5	H_2O	K_2CO_3	80	2	37
6	Ethanol/ H_2O ^c	K_2CO_3	80	2	77
7	DMF/ H_2O ^d	CS_2CO_3	80	2	86
8	DMF/ H_2O	Na_2CO_3	80	2	79
9	DMF/ H_2O	Et_3N	80	2	56
10	DMF/ H_2O	NaOAc	80	2	69
11	DMF/ H_2O	NaOH	80	2	73
12	DMF/ H_2O	K_2CO_3	80	0.5	21
13	DMF/ H_2O	K_2CO_3	80	1	44
14	DMF/ H_2O	K_2CO_3	80	1.5	83
15	DMF/ H_2O	K_2CO_3	20	2	trace
16	DMF/ H_2O	K_2CO_3	40	2	36
17	DMF/ H_2O	K_2CO_3	60	2	57
18	DMF/ H_2O ^e	K_2CO_3	80	2	38
19	DMF/ H_2O ^f	K_2CO_3	80	2	67
20	DMF/ H_2O	K_2CO_3	80	2	99

^a Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), catalyst (Pd-Cu NWs, 4 mg).

^b Solated yields.

^c EtOH/ H_2O = 1:1.

^d DMF/ H_2O = 1:1.

^e Catalyst (Pd-Cu NWs, 1 mg).

^f Catalyst (Pd-Cu NWs, 2 mg).

thesis [37]. The Cu 2p XPS spectra (Fig. 2D) reveal the co-existence of Cu^0 and Cu^{2+} species in Pd-Cu NWs [38], while the content of the former is much higher than that of the latter [39].

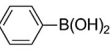
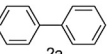
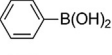
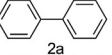
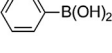
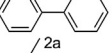
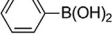
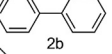
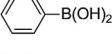
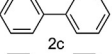
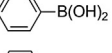
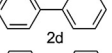
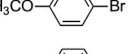
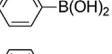
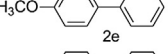
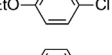
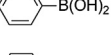
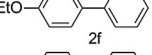
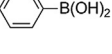
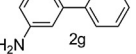
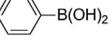
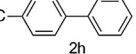
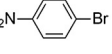
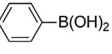
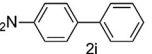
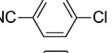
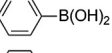
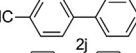
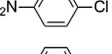
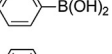
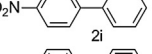
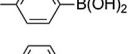
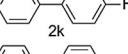
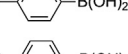
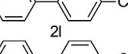
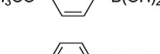
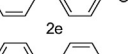
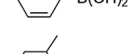
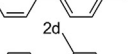
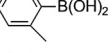
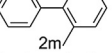
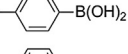
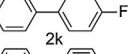
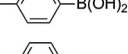
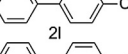
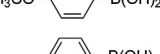
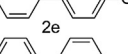
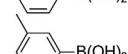
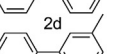
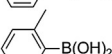
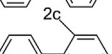
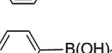
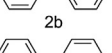
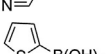
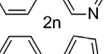
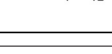
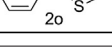
To elucidate the role of NP-40 in the formation of Pd-Cu NWs, we investigated the effects of NP-40 in the synthetic system. The absence of NP-40 yields agglomerated nanoparticles (Supporting Information, Fig. S1A). Increasing the amount of NP-40 (Supporting Information, Fig. S1B,C) improves the dispersity of the resulting products, along with the emergence of wire-like structures at 0.15% NP-40 (Supporting information, Fig. S1C). At NP-40 of 0.2%, the products contain mainly well-defined nanowires with high dispersity (Fig. 1). It indicates the pivotal role of NP-40 as a structure-directing and stabilizing agent to induce the formation of nanowires and prevent the nanoparticles agglomeration [25,40].

3.2. Catalytic activities in suzuki cross-coupling reactions

We tested the catalytic performance of Pd-Cu NWs in the Suzuki cross coupling reaction, which is a powerful strategy for the synthesis of C–C bonds in the production of medicine, agrochemicals, fragrances, and engineering materials [4,41,42]. As well known, there are various influencing factors in a Suzuki cross coupling reaction, such as base, solvent, temperature, and reaction time [43]. Accordingly, we tested the catalytic activity of Pd-Cu NWs and compared the results with those of Pd NPs commonly used for the Suzuki cross coupling reaction [43]. The specific procedure for the Suzuki cross coupling reactions, the relevant physical properties and the copies of 1H and ^{13}C NMR spectra for the products are provided in ESI.

Phenylboronic acid and bromobenzene were employed for screening the reaction parameters (Table 1). First, various solvents were tested (Table 1, entries 1–7). Since water is safe, readily available, and environment-benign [44,45], we used water to reduce the amount of organic solvent used in the reaction. It is observed

Table 2
The scope of substrates^a.

Entry	Aryl halide	Arylboronic acid	Products	Time (h)	Yield (%) ^b
1			 2a	2	99
2			 2a	2	94
3			 2a	2	94
4			 2b	2	90
5			 2c	2	93
6			 2d	2	98
7			 2e	2	99
8			 2f	4	90
9			 2g	4	83
10			 2h	4	85
11			 2i	4	83
12			 2j	4	81
13			 2i	4	79
14			 2k	2	91
15			 2l	2	90
16			 2e	2	96
17			 2d	2	98
18			 2m	2	72
19			 2k	2	91
20			 2l	2	90
21			 2e	2	96
22			 2d	2	98
23			 2c	2	92
24			 2b	2	88
25			 2n	4	78
26			 2o	6	82

^aReaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), catalyst (Pd-Cu NWs, 4 mg).

^bSolated yields.

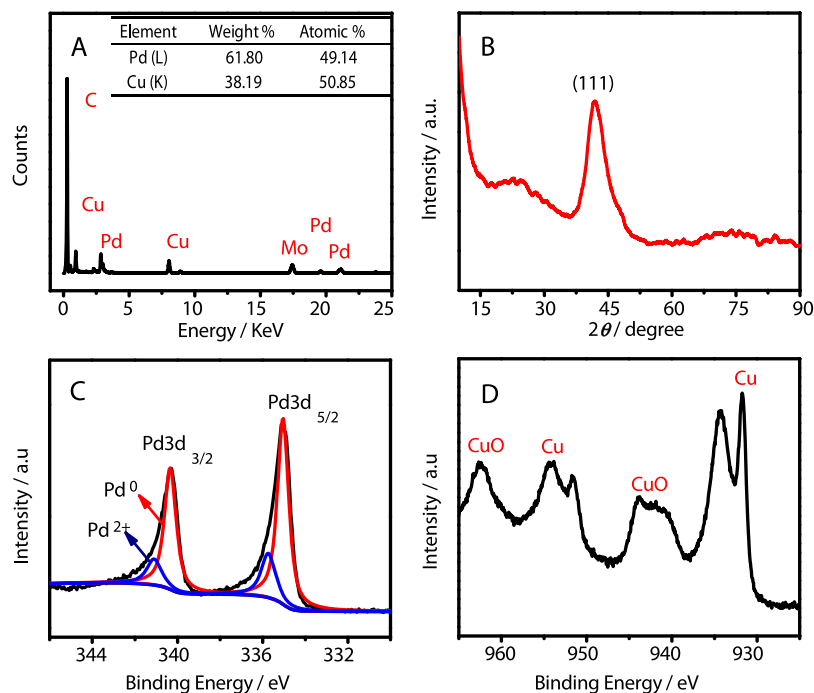


Fig. 2. EDS (A), XRD (B), high-resolution Pd 3d (C) and Cu 2p (D) XPS spectra of Pd-Cu NWs.

that the reaction in DMF/H₂O (1:1) gives biphenyl in excellent yield (Table 1, entry 1) as a result of high dispersion of reactants in DMF and good solubility of the bases in water [46]. Meanwhile, the impact of different bases on the efficiency of this process was studied (Table 1, entries 8–12) [47]. It is found that K₂CO₃ exerts most effectively for the Suzuki cross coupling reaction, superior to Na₂CO₃, Et₃N, Cs₂CO₃ and other bases. Therefore, we adopted K₂CO₃ as base for the Suzuki cross coupling reaction.

As for the effects of reaction time, there is gradual increase of the product yield with prolonged reaction time (Table 1, entries 13–15), and highest yield was obtained after 2 h. Next, the effects of temperature were investigated. It was noticed that (Table 1, entries 16–18) there is significant decrease of product yield when the reaction temperature is below 25 °C (Table 1, entry 16). Furthermore, the results of dosage variation (Table 1, entries 19–20) reflect the essential role of the Pd-Cu NWs catalyst for product yield.

According to the data acquired so far, the optimized reaction conditions are determined as: stirring a mixture of aryl halide (0.5 mmol, 1 equiv), phenylboronic acid (0.6 mmol, 1.2 equiv), K₂CO₃ (1 mmol, 2 equiv), Pd-Cu NWs (4 mg), and 2 mL of DMF/H₂O (v/v = 1/1) in a Schlenk tube (10 mL) at 80 °C for 2 h.

We observed that phenyl iodide, chloride, and fluoride react efficiently with phenylboronic acid under the optimized experimental conditions (Table 2, entries 1–3), but there is considerable difference in product yield. The activation of C–X bonds follows the sequence of I > Br > Cl > F [48,49]. As for the influence of steric hindrance, the results obtained based on the mono-substituents on the aryl bromide show a sequence of *para* > *meta* > *ortho*. Specifically, productivity is better for *para*-bromotoluene in comparison with those of *meta*-bromotoluene and *ortho*-bromotoluene (Table 2, entries 4–6), owing to the steric hindrance effects of the reactants [50].

Then, several functionalized aryl bromides and phenyl boronic acids containing electron-donating and electron-withdrawing groups such as –OCH₃, –OEt, –NH₂, –CN, –NO₂, –CHO, –F, and –Cl were examined to demonstrate the versatility of Pd-Cu NWs for the Suzuki cross coupling reaction. The results show moderate to excellent yields of the corresponding products (Table 2, entries 7–24).

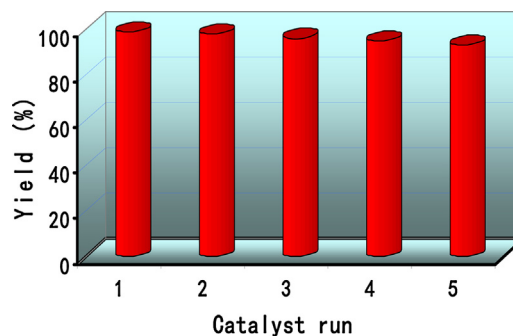


Fig. 3. The recycling test of Pd-Cu NWs for the Suzuki cross coupling reaction.

Encouraged by the efficiency of the protocol, the reaction of aryl-substituted pyridine was examined, which is the most common *N*-heteroaryl units in pharmaceutically active compounds (Table 2, entry 25–26). The results reflect lower reaction activity and reaction rates. This is presumably due to the partial carbonization of substrates [51].

The recyclability of Pd-Cu NWs in the Suzuki cross-coupling reaction between bromobenzene and phenylboronic acid was tested. The catalyst was separated by sample filtration, and despite small there was certain loss of catalyst in the recycling process. To ensure the same amount of catalyst in each run of the recycling experiment, we conducted in parallel several sets of the experiment under identical conditions. The reaction of the target set was supplemented with catalyst from the other parallel sets to make sure the scale of catalyst is 4 mg in each run. It was found that Pd-Cu NWs still display high product yield of 93% at the fifth run (Fig. 3). According to the TEM images, the morphology of the Pd-Cu NWs observed after the reaction is similar to that of the freshly prepared one (SI, Fig. S2). The remarkable catalytic activity and stability of Pd-Cu NWs can be ascribed to the unique and stable wire-like nanostructures [52], along with the felicitous synergistic effects between Pd and Cu [53].

4. Conclusions

We synthesized Pd-Cu NWs by a facile and efficient one-pot wet-chemical method. The unique structure of Pd-Cu alloy is essential for its high catalytic activity in the Suzuki cross coupling reaction under mild conditions. And the Pd-Cu NWs catalyst is stable and can be reused, showing 93% conversion at the fifth run. The Pd-Cu NWs system shows the efficiency and reusability of a heterogeneous catalyst, providing a promising platform for broadening the application of Pd-based catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2016.02.015>.

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