

Development of Hierarchical Polymer@Pd Nanowire-Network: Synthesis and Application as Highly Active Recyclable Catalyst and Printable Conductive Ink

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A facile one-pot approach for preparing hierarchical nanowire-networks of hollow polymer@Pd nanospheres is reported. First, polymer@Pd hollow nanospheres were produced through metal-complexation-induced phase separation with functionalized graft copolymers and subsequent self-assembly of PdNPs. The nanospheres hierarchically assembled into the nanowire-network upon drying. The Pd nanowire-network served as an active catalyst for Mizoroki–Heck and Suzuki–Miyaura coupling reactions. As low as 500 $\mu\text{mol}\%$ Pd was sufficient for quantita-

tive reactions, and the origin of the high activity is ascribed to the highly active sites originating from high-index facets, kinks, and coalesced structures. The catalyst can be recycled via simple filtration and washing, maintaining its high activity owing to the micrometer-sized hierarchical structure of the nanomaterial. The polymer@Pd nanosphere also served as a printable conductive ink for a translucent grid pattern with excellent horizontal conductivity ($7.5 \times 10^5 \text{ S m}^{-1}$).

Introduction

Nanoscale hybridization of functional organic and inorganic components realizes a spectrum of applications, which rely on the design of well-defined, multifunctional materials. Noble-metallic nanoparticles (NPs) have been important constituents for such hybrid materials because of their excellent applicability in catalysis, gas sensors, energy conversion and fuel cells, surface-enhanced Raman scattering, and printable conductive ink.^[1] The large surface-to-volume ratios and specific crystalline structures of NPs result in a large share of atoms located on the surface, which can significantly influence the material properties.^[2,3] For example, in catalysis, ultrafine NPs are typically more reactive than bulk metal counterparts. However, they are prone to aggregation due to high surface energy, and recovering of NPs after completion of the reaction by simple filtration is difficult. Over the past decade, research into the development of hierarchical nanostructures has focused on ensuring higher activity and reusability, especially for Pd nanoparticle (PdNP) catalysts.^[4–5]

Hollow spherical nanostructures form a unique class of hierarchical architectures due to their high specific surface areas, enabling high metal payload and excellent catalytic activity.^[6] However, most of these approaches are prone to catalyst

leaching or degradation from repeated cycles, thus impairing the reaction yields and limiting the reuse. Moreover, multistep modifications such as chemical etching and thermolysis create additional problems of processes and energy costs. Therefore, exploration of facile and efficient methods to design and fabricate such hierarchical structures for PdNPs is of critical importance. Another important potential applications of noble metals is in fabrication of conductive materials by printed electronics.^[7–8] These printed materials are employed in photovoltaics, transistors, displays, batteries, antennas, and sensors.^[8] However, metal NPs in conductive inks are typically stabilized by surfactants and polymer additives. The stabilizers need to be removed before or during the sintering process, either by bulk heating or selective welding,^[9] in order to decrease the resistance at the junction. Printed patterns of Pd⁰ were applied as metallization catalysts for conductive patterns, since Pd⁰ is an excellent catalyst for electroless plating of various metals.^[10–12] Typically, fabrication of Pd⁰ patterns requires reduction of Pd²⁺ photocatalyst printed on suitable substrates.^[13]

Herein, we present a unique functionalized graft copolymer, poly(NVK-co-MAH)-*g*-(NH-(PPO₁₀-co-PEO₃₁)) [NVK = *N*-vinylcarbazole, MAH = maleic anhydride, PPO = polypropylene oxide, PEO = polyethylene oxide], which facilitates controlled assembly of ultrafine PdNPs. We also report its application to Mizoroki–Heck and Suzuki–Miyaura reactions, where the quantitative production of coupling compounds was achieved with trace (500 $\mu\text{mol}\%$) Pd. Furthermore, the catalyst could be easily recycled for at least five cycles without the loss of high activity. Inkjet printing of the polymer@Pd nanosphere ink produced a translucent and highly conductive pattern.

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Results and Discussion

In the approach taken here, a functionalized graft copolymer, poly(NVK-co-MAH)-*g*-(NH-(PPO₁₀-co-PEO₃₁)) (Scheme S1 in the Supporting Information), was used to produce extended well-formed polymer@Pd nanowire networks. In a typical synthesis, a 120 μM (CF₃COO)₂Pd/-tetrahydrofuran (THF) solution (2 mL) was added to a 40 μM poly(NVK-co-MAH)-*g*-(NH-(PPO₁₀-co-PEO₃₁))-THF solution under an N₂ atmosphere. The mixture was stirred for 1 h at room temperature. For reduction of Pd²⁺, NaBH₄ in methanol (4 mL, 4 mole equiv to Pd) was subsequently added under an N₂ atmosphere, and the solution was stirred for 1 h. The resulting complex solution was poured into methanol, and the precipitate was filtered and dried under vacuum. The Pd content incorporated onto the hollow spheres was estimated as 21 wt% by thermogravimetric analysis (Figure S2 in the Supporting Information).

Figure 1 shows electron microscopic images of the material generated according to this strategy. The samples were prepared by spin-casting a THF solution of the product (3 mg mL⁻¹) on aluminum foil and copper grids with carbon coating for scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The SEM image (Figure 1 a) shows a networked structure consisting of spherical particles with the average diameter of about 100 nm. The magnified SEM image (Figure 1 b) shows raspberry-like spheres consisting of PdNPs with the average diameters of about 8 nm connected to each other to form the networked structure. The spheres are hollow, as shown in Figure 1 b including a sphere with defects.

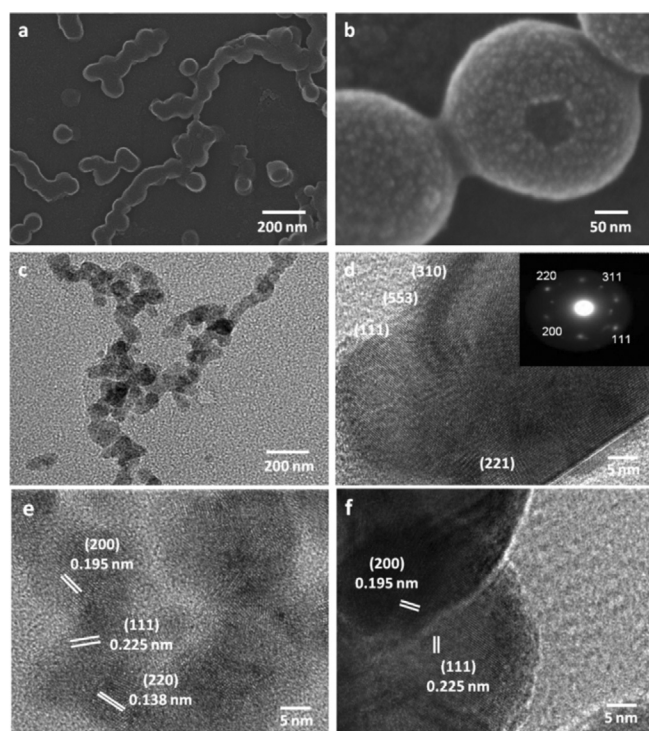


Figure 1. SEM (a, b), TEM (c), HRTEM (d–f), and selected area electron diffraction (SAED) pattern (inset in d) images of the Pd nanowire-network.

TEM analysis was performed to investigate the assembly of the PdNPs on the hollow spheres. It is quite evident from Figure 1 c that the PdNPs have coalesced with each other, which is a result of strong interactions. The scanning tunneling electron microscopy (STEM) image (Figure S3 in the Supporting Information) also shows that the PdNP layer has grown over the polymer shell, producing closed nanoshells, interconnected in the nanowire-network fashion. It should be mentioned that uncontrolled aggregation leading to large clusters did not occur despite the strong interactions between PdNPs. The nanowire-network is two-dimensional, as confirmed by the atomic force microscopy (AFM) image (Figure S3).

The Pd in the nanowire-network is almost monocrystalline, as confirmed by the selected area electron diffraction (SAED) pattern (inset in Figure 1 d), which shows clear spots. The Pd nanowire-network contains (553),^[14fg] (310),^[14c] (111),^[14c,e,g] and (221)^[14c,g] high-index facets along the border as shown in Figure 1 d.^[4a,5g,14] Various defective crystalline structures were also observed in the high-resolution (HR) TEM images. Figure 1 e indicates the presence of kinks formed between the coalescence of Pd nanoparticles, which increase the coarseness of the nanostructure. Figure 1 f shows twined (111) and (200) planes originated from the coalescence of the PdNPs. Figure S5 in the Supporting Information shows the intrafacial dislocation in the lattice planes. These characteristic structures such as high-index facets are known as very reactive sites enhancing the catalytic performance of the Pd⁰ material as described later.

The powder X-ray diffraction (XRD) pattern of this network (Figure 2) also shows peaks assignable only to fcc Pd (JCPDS

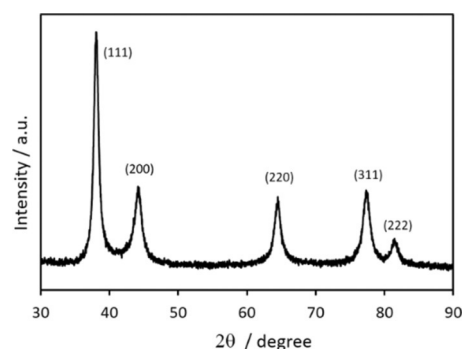


Figure 2. X-ray diffraction (XRD) pattern of the Pd nanowire-network (Cu-K_α).

no. 05-0681), indicating the presence of pure metallic Pd crystals. The sharp (111) peak also provides evidence of pure crystallinity. The crystallite size was estimated as 10 nm from the full width at half maximum (FWHM) of the (111) diffraction by applying Scherrer's equation ($D = \kappa \lambda / \beta \cos \theta$, where D is the average particle size in Å, β is FWHM of the diffraction peak in radian, θ is the peak position ($2\theta = 38^\circ$), λ is the wavelength of the radiation (1.54056 Å for Cu-K_α radiation), and κ is the shape factor of 0.89 for spherical crystals). The identical sizes that were calculated from the SEM image and the XRD diffraction also support the monocrystalline nature.

A plausible mechanism for the formation of the Pd nanowire-network is illustrated in Figure 3. The functionalized graft

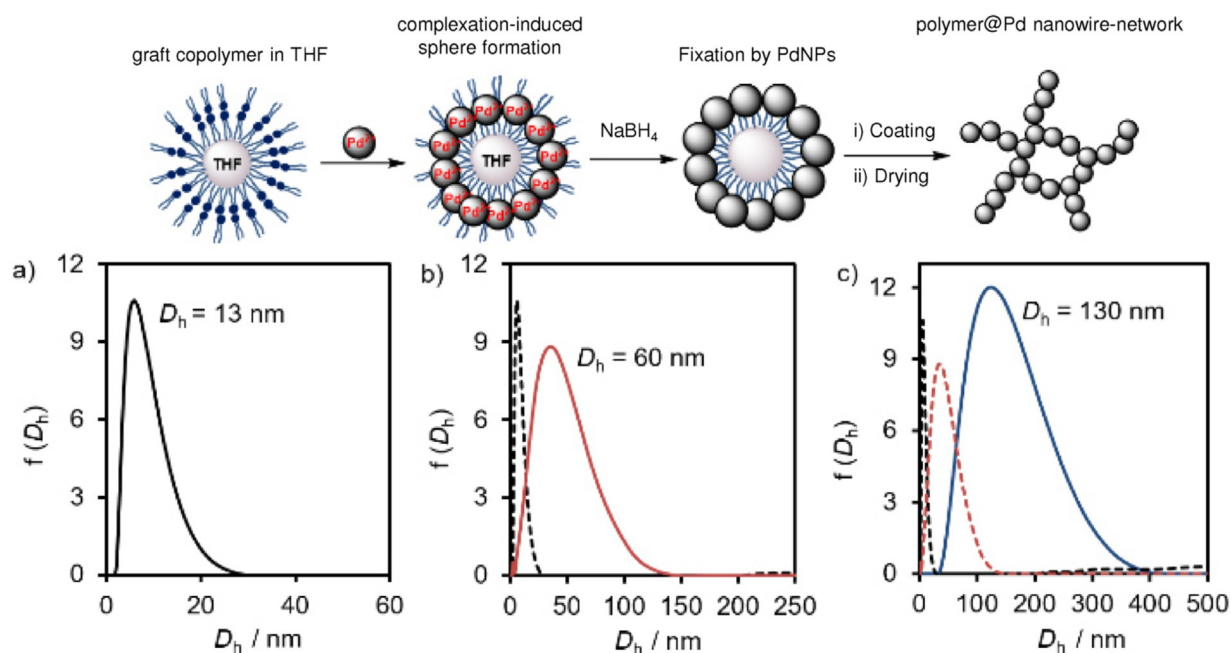


Figure 3. Plausible mechanism of hollow sphere formation with dynamic light scattering (DLS) profiles in THF.

copolymer poly(NVK-co-MAH)-*g*-(NH-(PPO₁₀-co-PEO₃₁)), carries carboxylic acid groups capable of coordinating with Pd²⁺ ions. The resulting ionic structure around the stem chain has poor affinity with THF, whereas the polyether chains have high affinity with THF. This difference in affinity promotes complexation-induced phase separation to form nanosized vesicles. Chemical reduction with NaBH₄ produces PdNPs from Pd²⁺ embedded on the sphere as seeds, forming polymer@Pd nanospheres. The dynamic light scattering (DLS) profiles in Figure 3 support this mechanism. The hydrodynamic diameter (D_h) of poly(NVK-co-MAH)-*g*-(NH-(PPO₁₀-co-PEO₃₁)) in THF is 13 nm (Figure 3a), and the complexation with Pd²⁺ results in an increase of D_h to 60 nm (Figure 3b), due to the electrostatic repulsion forces between Pd²⁺ ions. The NP formation via reduction concentrates the Pd²⁺ in solution onto the sphere surface, thus leading to their expansion ($D_h=130$ nm) (Figure 3c). Upon drying, the stiff shell consisting of PdNPs maintains its shape, whereas the inner polyether chain shrinks towards the shell. As a result, hollow particles are produced. The self-assembly of PdNPs into the nanowire-network can be ascribed to the strong interparticle interactions originating from the high surface energy and elasticity of PdNPs.^[15]

We then employed the Pd nanowire-network to the Mizoroki–Heck (Table 1) and the Suzuki–Miyaura coupling (Table 2) reactions, since these reactions have excellent applications in synthetic organic chemistry and the fabrication of electronic materials.^[15,16] First, the Mizoroki–Heck reaction of iodobenzene (**1a**) and *n*-butyl acrylate (**2**) was carried out with the nanowire network (500 μmol% of Pd to **1a**) in 1-butanol in the presence of triethylamine (Et₃N) for neutralization and tetrabutylammonium acetate (TBAA)^[17] as an efficient base at 100 °C. The coupling proceeded smoothly to give *n*-butyl cinnamate (**3a**) in a 98% yield (entry 1, Table 1). The reactions of **1a** and *p*-

Table 1. Mizoroki–Heck reaction with polymer@Pd nanowire-network.

Entry	1 or 4 [R ¹]	Alkene [R ²]	3	Yield [%]
1 ^[a]	1a (H)	2 (CO ₂ Bu ⁿ)	3a	98
2 (2nd use) ^[a,d]	1a (H)	2 (CO ₂ Bu ⁿ)	3a	98
3 (4th use) ^[a,d]	1a (H)	2 (CO ₂ Bu ⁿ)	3a	97
4 (5th use) ^[a,d]	1a (H)	2 (CO ₂ Bu ⁿ)	3a	97 ^[c]
5 ^[a]	1a (H)	2' (Ph)	3'a	99
6 ^[a]	1b (CH ₃ O)	2' (Ph)	3'b	85
7 ^[b]	4a (H)	2' (Ph)	3'a	85
8 ^[b]	4b (CH ₃ O)	2' (Ph)	3'b	90
9 ^[b]	4c (CH ₃ CO)	2' (Ph)	3'c	95
10 ^[b]	4d (CHO)	2' (Ph)	3'd	92

[a] **1** (1.0 mol equiv), **2** (2.0 mol equiv), Et₃N (3.0 mol equiv), tetrabutylammonium acetate (TBAA, 0.2 mol equiv), Pd (500 μmol%), 1-BuOH, 100 °C, 24 h. [b] **4** (1.0 mol equiv), **2'** (2.0 mol equiv), NaOAc (0.6 mol equiv), tetrabutylammonium bromide (TBAB, 0.2 mol equiv), Pd (500 μmol%), 100 °C, 24 h. [c] Pd concentration detected by ICP-MS in the supernatant of the reaction mixture was below 1 ppb. [d] The catalyst was recycled by filtration and washing with EtOAc.

methoxy iodobenzene (**1b**) with styrene (**2'**) also proceeded smoothly to give the corresponding stilbenes, **3'a** and **3'b**, in 85 and 99% yields (entries 5 and 6), respectively. Moreover, aryl bromides may also be used as substrates for this coupling. When the reaction of bromobenzene (**4a**) and **2'** was performed in the presence of sodium acetate and tetrabutylammonium bromide (TBAB), the reaction gave **3'a** in an 85%

Table 2. Suzuki–Miyaura cross-coupling reactions with polymer@Pd nanowire-network.^[a]

Entry	1, 4, 6 [R ¹]	Time [h]	5	Yield [%]
1	4 a (H)	6	5 a	> 99
2 (2nd use)	4 a	6	5 a	98
3 (4th use)	4 a	6	5 a	97
4 (5th use)	4 a ^[c]	6	5 a	95 ^[b]
5	1 a (H) ^[c]	6	5 a	98 ^[b]
6	4 b (CH ₃ O)	6	5 b	99
7	4 c (COCH ₃)	4	5 c	99
8	4 e (NO ₂)	4	5 d	99
9	4 f (CH ₃)	6	5 e	99
10	1 g (OH)	8	5 f	96
11	6 a (H)	6	5 a	90
12	6 b (CH ₃ O)	6	5 b	95
13	6 c (COCH ₃) ^[c]	6	5 c	95 ^[b]

[a] Reaction conditions: phenylboronic acid (0.55 mmol), aryl bromide (0.50 mmol), K₂CO₃ (2 equiv), tetrabutylammonium bromide (TBAB, 5 μmol%), Pd (500 μmol%), EtOH/H₂O (v/v = 1/1), 80 °C [b] Pd concentration detected by ICP-MS in the supernatant of the reaction mixture was below 1 ppb [c] The catalyst was recycled by filtration and washing with EtOAc.

yield. Both electron-rich and electron-deficient aryl bromides (**4 b–d**) may also be reacted with **2 b** to give the corresponding cinnamates, **3' b–3' d**, in 90–95% yields (entries 7–10). We ascribed the excellent catalytic activity enabling catalysis with trace amounts of Pd to the characteristic structures such as high-index facets observed in the HRTEM images.

The Suzuki–Miyaura coupling reaction was also examined with the polymer@Pd nanowire-network (Table 2). We used **4 a** and phenylboronic acid as the initial substrates. This cross-coupling reaction was also carried out using 500 μmol% of the Pd nanowire-network as the catalyst in a mixed solvent of water and ethanol (v/v = 1/1) under reflux conditions. The yield was only 53% but was enhanced considerably to > 99% by the addition of 5 μmol% TBAB (run 1), served as a phase transfer catalyst.^[18,20d] Table 2 shows that the nanowire-networks are highly active for various electron-rich and electron-deficient aryl bromides in a similar manner as the Mizoroki–Heck reaction (entries 5–9). Moreover, less reactive aryl chlorides may also be used as the substrates for this coupling. Cross-coupling reaction of chlorobenzene (**6 a**) and phenylboronic acid was performed under identical conditions, and the reaction gave **5 a** in 90% yield. Both electron-rich and electron-deficient chlorides (**6 b–c**) may also be reacted to give the corresponding biphenyls, **5 b–5 c**, in 95% yields. Figure S6 and S7 in the Supporting Information show plots of conversion versus reaction time for the Mizoroki–Heck and Suzuki–Miyaura reactions, in which the conversions increase with time reaching quantitative yields in 24 and 6 h, respectively.

The high activity of the polymer@Pd nanowire-network towards aryl chlorides identical to the aryl bromides and aryl iodides can be presumably ascribed to the steric restrictions on approach of the substrates towards the Pd nanowire-network.^[19] The affinity of the polymer@Pd nanowire-network towards the reaction solvents and the substrates, for example, 1-BuOH, EtOH/H₂O, and bromobenzene, is very low as confirmed by the negligible swelling ratios (< 5%). This low affinity, made the approach as the rate-determining step in spite of the excellent chemical activity originating from the high active sites. This low affinity of the polymer@Pd nanowire-network is also a possible reason for the improvement of the yield by the addition of TBAB.

Since the nanowire-network efficiently promoted the Mizoroki–Heck and Suzuki–Miyaura coupling reactions, recycling of the polymer@Pd nanowire-network was investigated for both reactions under identical conditions. After the reactions in entries 1 of Tables 1 and 2 were completed, the nanowire-network was recovered by simple filtration and washing with ethyl acetate owing to the microscaled size, and reused for the identical reactions. The catalysts of both reactions were reused five times without the loss of catalytic activity, as indicated in entries 2–4 in both Tables 1 and 2. The negligible leaching of Pd species was confirmed in the reaction mixtures after the 5th reuse cycles of the Pd network catalysts by inductively coupled plasma-mass spectrometry (ICP-MS) analysis (entries 4 in Tables 1 and 2). The concentrations of Pd species in the supernatants of both reactions were ≤ 1 ppb, which is as low as the ICP-MS detection limit and lower than previously reported catalyst systems that plausibly proceeded with ppm-order of leached Pd species.^[20] The ease of redeployment of the catalyst and the quantitative conversions over several efficient cycles testifies to the versatility of the Pd nanowire-network as an active immobilized catalyst.

A hot filtration test was conducted to investigate the leaching behavior for the reaction of the **4 a** and phenylboronic acid conducted under identical conditions with entry 1 in Table 2 (Figure S8 in the Supporting Information).^[21] The reaction mixture was hot-filtered at 80 °C after 1 h to remove the insoluble Pd network. As a result, the conversion of **4 a** stayed constant at 55% after filtration. The ICP-MS analysis and the hot filtration test manifested negligible leaching. Moreover, the TEM images of the reused catalysts (Figure S9 and S10 in the Supporting Information) indicate that the Pd nanowire-network maintained the tertiary nanostructure during the reactions. These results indicate that this catalysis proceeded on the surface of the PdNPs or with the undetectable amount of leached Pd species, which was quantitatively captured via release–catch mechanism.^[22] Heterogeneous catalysts often suffer from leaching of the active metal species during reactions, and eventually lose their catalytic activity. Leaching is also responsible for product contamination with metals and loss of the noble metal. The negligible leaching of Pd species from this catalyst is an important advantage for maintaining high catalytic activity, as well as avoiding outflow of and contamination by Pd.

The polymer@Pd nanosphere was also applied as a conductive ink. The polymer@Pd nanospheres ink in THF (20 mg mL⁻¹) was prepared by dispersing the polymer@Pd nanosphere isolated via precipitation into methanol. The ink was stable up to one week without aggregation. The resulting ink was inkjet-printed on a cleaned glass substrate as a grid pattern with a 50 μm spacing and a 15 μm line width in a 1×1 cm square (Figure 4a). Figure 4b shows the printed Pd nanowire-network grids on a text, indicating the excellent visibility. The hybridization with the graft copolymer realized printing of the narrow pattern with the stable ink. The printed patterns showed excellent horizontal conductivity of 7.5×10⁵ S m⁻¹ owing to the efficient connection of PdNPs existing on the shell even without annealing or removal of the organic parts.

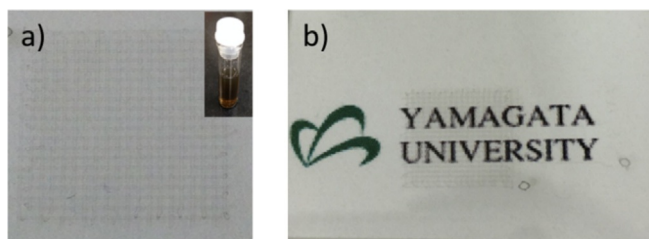


Figure 4. Optical images of inkjet-printed grids (1×1 cm squares) of polymer@Pd nanosphere ink on glass substrate: a) magnified image with inset image of the ink and b) visibility of the university logo underneath the printed square-grids of polymer@Pd nanosphere.

Conclusion

We have successfully developed a polymer@Pd nanowire-network material by utilizing poly(NVK-co-MAH)-g-(NH-(PPO₁₀-co-PEO₃)) as the template for complexation-induced phase separation and spontaneous coassembly. A well-controlled hierarchical nanostructure was constructed via connection of hollow spheres comprising PdNPs. This Pd nanowire-network has the advantages of a facile preparative protocol, excellent catalytic activity and recyclability in Mizoroki–Heck and Suzuki–Miyaura coupling reactions, and application for printable and conductive materials. We anticipate that this facile fabrication procedure can be extended to the fabrication of various nano hybrid materials with designed functionalities for catalysis, energy applications, and printable electronics.

Experimental Section

Complete experimental procedures, extra schemes, HRTEM, SPM, STEM, kinetic profiles, hot filtration test, and polymer@Pd nanosphere conductive ink preparation can be found in the Supporting Information.

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Keywords: hollow nanoparticles • immobilized catalysts • Pd nanowire-network • printable conductive ink • self-assembly

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