Enhanced Catalytic Activity in Suzuki–Miyaura Couplings by Shell Crosslinked Pd Nanoparticles from Alkene-terminated Phosphine Dendron-stabilized Pd Nanoparticles

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New alkene-terminated phosphine dendron-protected palladium nanoparticles (NPs) have been synthesized, and the olefin metathesis polymerization of their Pd NPs led to shell crosslinked Pd NPs without aggregation of the Pd NPs. The introduction of crosslinking at the surface of the protective ligand enhanced the catalytic activity of the Pd NPs for Suzuki– Miyaura couplings.

Metal nanoparticles (NPs) have been the focus of significant interest because of their unique electronic, optical, and catalytic properties.¹ Control of the surface properties and reactivity of the metal NPs is an important aspect of developing nanomaterial applications. The size, shape, and surface properties of metal NPs are crucially controlled by the nature of the protective ligand shells. The preparation of uniform metal NPs has been intensively pursued because of their applications as nanocatalysts in organic transformations such as carbon-carbon bondforming reactions.^{2,3} Specifically, palladium NPs have become of increasing scientific interest as catalysts for the Suzuki-Miyaura cross-coupling reaction, which is among the most powerful methods in organic synthesis.³ As an example, we reported that optically active 2,2'-bis(diphenylphosphino)-1,1'binaphthyl-stabilized palladium NPs catalyzed asymmetric Suzuki-Miyaura cross-coupling reactions at room temperature.⁴ The development of a generalized method for the fabrication of multifunctional nanocatalysts remains an important and challenging issue.

There has been a fundamental interest in the surface modification of gold NPs by the crosslinking of alkene groups around the periphery of gold NPs stabilized by thiol ligands with the alkene groups via alkene metathesis polymerization using Grubbs' catalyst.⁵ Although a number of studies on olefin metathesis of alkenethiol-stabilized gold NPs and the properties of shell crosslinked gold NPs have been reported, there is no report concerning the olefin metathesis of palladium NPs stabilized by alkene-terminated phosphine dendrons and the catalytic activity of shell crosslinked palladium NPs.

In our recent research, special emphasis has been placed on the elucidation of the structural driving forces in order to control the particle size and shape and the reactivity of the phosphine dendron-stabilized metal NPs. The key structural elements of the new phosphine dendrons **1** and **2**, having a long alkyl chain at the focal point in Figure 1, as protective ligands in this study consist of triphenylphosphine for the coordination site and an alkene group for the metathesis polymerization site.⁶ We have found that the alkene-terminated phosphine dendron-stabilized palladium NPs, **1**–Pd NPs and **2**–Pd NPs, have a smaller core size and narrower size distribution (2.2 ± 0.3 nm for **1**–Pd NPs and 1.9 ± 0.3 nm for **2**–Pd NPs) and that the olefin metathesis polymerization of the **1**–Pd NPs or **2**–Pd NPs led to the shell



Figure 1. Structures of 1 and 2. Phosphine dendrons 1 and 2 used to derive the palladium NPs, 1–Pd and 2–Pd NPs.



Scheme 1. Crosslinking of the peripheral alkene groups of **1**–Pd NPs by olefin metathesis.

crosslinked palladium NPs, poly-1-Pd NPs and poly-2-Pd NPs, without aggregation of the palladium NPs (Scheme 1). Ideally, the shell crosslinked Pd NPs should be surrounded by a nonadherent coating, or nanocapsule, that prevents aggregation of the Pd NPs, permits passage of the catalyst substrate and product, but does not adversely affect the catalytic properties. These properties could promote the activity of the nanoparticle catalysts. Interestingly, we have found that the noncrosslinked Pd NPs, 1-Pd NPs and 2-Pd NPs, and the shell crosslinked Pd NPs, poly-1-Pd NPs and poly-2-Pd NPs, showed very different catalytic activities for the Suzuki-Miyaura cross-coupling reactions, although they have similar diameters of 1.9-2.2 nm. Generally, the catalytic activities of metal NPs depend on the particle size. This communication presents the fabrication of shell crosslinked Pd NPs, poly-1-Pd NPs and poly-2-Pd NPs, as multifunctional metal-incorporated nanocapsules with enhanced catalytic activities for Suzuki-Miyaura couplings by shell crosslinked Pd NPs.

A typical procedure for the preparation of the Pd NPs, 1-Pd NPs, is as follows: To a vigorously stirred solution of $K_2[PdCl_4]$ (65 mg, 0.2 mmol) in 7 mL of deionized water was added phosphine 1 (330 mg, 0.4 mmol) in 30 mL of THF. NaBH₄



Figure 2. (a) TEM image and distribution of 1–Pd NPs $(2.2 \pm 0.3 \text{ nm})$. (b) TEM image and distribution of poly-1–Pd NPs $(2.1 \pm 0.3 \text{ nm})$.

(80 mg, 2 mmol) in 5 mL of deionized water was then added. The mixture was stirred for 1 h at room temperature. After the reaction, the filtrate was evaporated in vacuo to yield the 1–Pd NPs. Purification (dichloromethane–diethyl ether) of the 1–Pd NPs was repeated until no free phosphine remained, as detected by TLC and ¹H and ¹³C NMR spectroscopy. The 1–Pd NPs are remarkably stable both in solution and the solid state. The 2–Pd NPs were prepared by the same procedure.

The particle size and size distribution of the 1–Pd NPs and 2–Pd NPs were analyzed by transmission electron microscopy (TEM). The core sizes of the NPs are small i.e., 2.2 ± 0.3 nm for the 1–Pd NPs (Figure 2a) and 1.9 ± 0.3 nm for the 2–Pd NPs (Figure 3a). The X-ray photoelectron spectroscopy (XPS) spectra of the 1–Pd NPs and 2–Pd NPs show that the binding energies for the Pd 3d doublet are 336.0 and 341.3 eV. There is a feature at 285 eV from C 1s and one at 132 eV from P 2p. There are no obvious surface plasmon bands in the UV–vis spectra of the 1–Pd NPs or 2–Pd NPs or 2–Pd NPs agrees with theoretical predictions⁷ and experimental observations for 2.2 nm alkane-thiolate-stabilized Pd NPs⁸ but not with the report of a 302 nm surface plasmon band for 2.2 nm octadecanethiolate-protected Pd NPs.⁹

The crosslinking of the alkene groups around the periphery of the 1–Pd NPs or 2–Pd NPs was achieved by Grubbs' metathesis as follows (Scheme 1):^{5,10} To a mixture of 1–Pd NPs (40 mg) in dry benzene (5 mL) was added a solution of the first generation Grubbs' catalyst¹¹ (20 mg) in dry benzene (95 mL) under an Ar atmosphere. The resulting mixture was stirred for 48 h at room temperature. After the reaction, the shell crosslinked palladium NPs, poly-1–Pd NPs, were purified using



Figure 3. (a) TEM image and distribution of 2–Pd NPs $(1.9 \pm 0.3 \text{ nm})$. (b) TEM image and distribution of poly-2–Pd NPs $(1.9 \pm 0.3 \text{ nm})$.



Scheme 2. Suzuki-Miyaura coupling reactions.

dichloromethane-hexane. Following the metathesis, the NPs remained soluble in benzene, dichloromethane, chloroform, tetrahydrofuran, acetone, ethyl acetate, dimethylformamide, dimethyl sulfoxide, and methanol. The poly-1-Pd NPs were analyzed by TEM and ¹HNMR spectroscopy. The TEM image of the poly-1-Pd NPs shows a core size of 2.1 nm, which indicates no aggregation of the palladium cores during the metathesis polymerization (Figure 2b). Analogously, no aggregation for the metathesis of the 2-Pd NPs was observed, as evidenced by the TEM image (Figure 3b). After the metathesis of the 1-Pd NPs, the ¹H NMR spectrum in Figure S1a⁶ shows that the terminal alkene proton resonances at δ ca. 5.1 and 5.8 as broad signals of 1-Pd NPs disappear and/or diminish and that a new broad peak appears at δ ca. 5.5 (Figure S1b),⁶ which corresponds to the internal alkene formed by the metathesis reaction.⁵ These findings indicate that crosslinking of the double bonds on the nanoparticle surface occurred. Similar ¹H NMR data were obtained for the poly-2-Pd NPs.

The catalytic activities of the palladium NPs (Ph₃Pstabilized Pd NPs, 1–Pd NPs, poly-1–Pd NPs, 2–Pd NPs, and poly-2–Pd NPs) dispersed in an organic solvent were tested in a very important carbon–carbon bond-forming reaction, the

Table 1. Suzuki–Miyaura couplings catalyzed by Pd NPs: Ph₃P–Pd, 1–Pd, poly-1–Pd, 2–Pd, and poly-2–Pd NPs^a

Entry	Catalyst, NPs	Halide	Boronic acid	Product	Yield /%
1	Ph ₃ P–Pd	3	4	5	19 ^b
2	1–Pd	3	4	5	33
3	poly -1 –Pd	3	4	5	86
4	2 –Pd	3	4	5	38
5	poly -2 –Pd	3	4	5	62
6	1–Pd	6	4	7	37
7	poly -1 –Pd	6	4	7	93
8	2 –Pd	6	4	7	34
9	poly -2 –Pd	6	4	7	71

^aReaction conditions: 1.0 mmol halide, 1.5 mmol boronic acid (4), 3 mmol KF, 0.01 mol % of Pd NPs, THF, 50 °C, and 20 h. ^bPh₃P-stabilized Pd NPs.

Suzuki-Miyaura coupling reaction. This choice was based on the fact that such a reaction provides a powerful tool for the synthesis of biaryls, which are found in many natural and synthetic products. Although it is known that Suzuki-Miyaura coupling reactions are carried out at reflux, we have carried out the Suzuki-Miyaura coupling reactions at 50 °C (Scheme 2).12 Typically, a mixture of 4-bromotoluene (3: 1.0 mmol) and phenylboronic acid (4: 1.5 mmol) in the presence of the triphenylphosphine (Ph₃P)-stabilized Pd NPs (diameter: 2 nm, 0.01 mol %) and KF (3 mmol) in anhydrous THF (2 mL) was stirred at 50 °C under argon for 20 h (Scheme 2-1). After workup, the crude products were purified by silica gel column chromatography (*n*-hexane:benzene = 1:1) to give the coupling product 5 in 19% yield (Table 1). The yield of the coupling product 5 increased to 33% when the 1-Pd NPs (diameter: 2.2 nm) were used as a catalyst (Table 1).¹³ In contrast to the 1– Pd NPs, a more significant improvement in the catalytic activity can be achieved by the shell crosslinked Pd NPs, poly-1-Pd NPs, i.e., the coupling product 5 was obtained in 86% yield using the poly-1-Pd NPs (diameter: 2.1 nm) (Table 1), although they have similar core sizes. Most notably, the yields in the reaction of 3 with 4 were remarkably influenced by the structure of the protective ligand on the noncrosslinked (1-Pd NPs) and crosslinked (poly-1-Pd NPs) NPs, even though the Pd NPs have very similar diameters (2.2 nm for 1-Pd NPs and 2.1 nm for poly-1-Pd NPs). Moreover, we found a similar catalytic activity of the 1-Pd NPs and 2-Pd NPs for the Suzuki-Miyaura couplings of 3 with 4 (Table 1); however, the poly-2-Pd NPs showed less catalytic activity than that of the poly-1-Pd NPs (Table 1). The above catalytic activities for the reaction of 3with 4 were similar to the results from the reaction of 6 with 4 using those Pd nanoparticle catalysts (Table 1). The shell crosslinked Pd NPs, poly-1-Pd NPs, acted as good catalysts for the bromide 6, having a longer alkyl-chain than the bromide 3, i.e., the reaction of 6 with 4 in the presence of poly-1-Pd NPs afforded the coupling product 7 in 93% yield under relatively mild conditions such as at 50 °C without reflux (Scheme 2-2) (Table 1). Notably, these findings indicate that the catalytic activities of the crosslinked Pd NPs, poly-1-Pd NPs and poly-2-Pd NPs, are higher than those of the noncrosslinked Pd NPs, 1-Pd NPs and 2-Pd NPs. Thus, we have found a considerable difference in the catalytic activities between the noncrosslinked and crosslinked Pd NPs. We are currently investigating the fundamental reasons for the observed differences in the catalytic activities.

In summary, shell crosslinked Pd NPs, poly-1–Pd NPs, were found to be versatile catalysts for the Suzuki–Miyaura coupling reactions under mild conditions. Remarkable differences in the catalytic activities of the crosslinked and noncrosslinked Pd NPs were found in the Suzuki–Miyaura couplings, although the Pd NPs have similar diameters. This aspect may have significant implications for the use of shell crosslinked Pd NPs as catalysts in organic reactions.

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