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Palladium nanoparticles stabilized by phosphine ligand for aqueous phase room temperature suzuki-Miyaura coupling

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ABSTRACT

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Keywords: Palladium nanoparticles Suzuki-Miyaura coupling Phosphine ligand Aqueous phase Room temperature Water soluble phosphine ligand triphenylphosphine-3,3',3"-trisulfonic acid trisodium salt (TPPTS) was used as the stabilizer as well as the activator to the palladium nanoparticles, which showed a high catalytic perfomance for aqueous phase Suzuki-Miyaura coupling reaction at room temperature.

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Introduction

Palladium nanoparticles (PdNPs), as one of the efficient catalysts for the Suzuki-Miyaura reaction, has attracted considerable attentions over last decades and the high catalytic efficiency, easy recyclability and low palladium residue have been achieved.¹ The general method for the fabrication of PdNPs catalyst is to immobilize the PdNPs on a support² or involve a capping agent to stabilize the colloid PdNPs.³ Thus, the catalytic performance of PdNPs is not only depended on the feature of nanoparticles but also affected by its supports or stabilizers.⁴ In most cases, the reactions catalysed by the PdNPs were performed in organic media. In order to make the organic synthesis or reactions more environmentally friend or green, it is strongly desirable that the reactions can be performed in aqueous media.

On the other hand, phosphine ligands, as one of efficient activators and stabilizers for palladium species, have achieved great success in homogenous and heterogeneous Suzuki-Miyaura coupling reaction.⁵⁻⁸ With this advantage, it has also drawn great interest to use the phosphine ligand to stabilize the PdNPs and perform the Suzuki-Miyaura reaction. For example, Fujihara et al utilized BINAP and Ph₃P as stabilizer for synthesis of PdNPs. The resulted PdNPs could well disperse in organic phase and catalyse the asymmetric Suzuki-Miyaura reaction. Both high reactivity and enantioselectivity were achieved.9 Fan et al reported that the phosphine dendritic polymer can be used as stabilizer for PdNPs, which was highly active for the catalysis of Suzuki-miyaura reaction.¹⁰ Lipshutz et al developed Fe-ppmPd NPs for sustainable Suzuki-Miyaura reaction, and found the phosphine ligand SPhos enhanced the catalysis activity significantly.¹¹ However, in all these cases, due to the ligands are organic soluble, a phase transfer process from water to organic phase is often needed during the preparation of PdNPs. In order to improve this situation, we aim to prepare a water dispersible yet highly efficient PdNPs with phosphine ligands as the capping agent.

phosphine We used a water soluble ligand triphenylphosphine-3,3',3"-trisulfonic acid trisodium salt (TPPTS) to cap the PdNPs and successfully obtained a waterdispersible phosphine stabilized PdNPs, as illustrated in Figure 1. Here, TPPTS was employed as the capping reagent and K₂PdCl₄ was used as the palladium source. Various reductants such as NH₂NH₂, NaBH₄, ascorbic acid and HCOONa were utilized for the synthesis of PdNPs catalysts. Depending on the reductants, the synthesized PdNps differed in their sizes. The obtained PdNPs were well dispersed in the water and can perform an aqueous phase Suzuki-Miyaura reaction at room temperature. Interestingly, the size of the PdNPs would significantly affect the catalytic efficiency and the best PdNPs catalyst was obtained by using HCOONa as the reductant.



Figure 1. Illustration the process for the synthesis of TPPTS stabilized PdNPs and their high catalytic performance for coupling reaction between 4-bromoanisole and phenylboronic acid.

Results and discussion

Experimental, TPPTS was firstly dissolved in the pure water (1 mg in 5 mL); and then K₂PdCl₄ was added under stirring at room temperature (500 µg in 0.5 mL of water). The reducing agents, NH₂NH₂, NaBH₄, ascorbic acid or HCOONa water solution (about 100 equivalents to K₂PdCl₄) was injected to the above mixture solution under stirring, respectively. The colour of solution turned into dark brown immediately with the adding of strong reducing agent NH₂NH₂ or NaBH4. The solution only turned into pale brown with the adding of ascorbic acid; and nearly no change in colour after adding of HCOONa. All of the mixture solutions were further aged for about 0.5 h, PdNPs were obtained. The resulted samples were subjected to TEM for morphology observation after subjected to dialyze for removing the excess salt. Figure 2 shows the TEM images of the resultant PdNPs capped with TPPTS. The size of nanoparticle was about 8.7 nm for NH₂NH₂ as the reductant (Fig.2A, named as PdNPs-NH₂NH₂). When NaBH4 was used as the reducing agent, the size of nanoparticles is broadly distributed and most of the nanoparticles are bigger than 3 nm (Fig.2B, named as PdNPs-NaBH4). The size of most of the PdNPs was larger than 2.5 nm for the ascorbic acid as reductant (Fig. 2C, named as PdNPs-Vc). A narrow distribution and size of 1.5 nm PdNP was obtained when HCOONa (Fig.2D, named as PdNPs-HCOONa) was as reducing agent. These results indicated that size of PdNPs could be regulated by the reducing capacity of agents. In addition, the precipitate was observed when PdNPs-NH2NH2, PdNPs-NaBH4 and PdNPs-Vc being stored in water more than two days. While PdNPs-HCOONa were still well dispersed in water solution even after one week. This indicated that TPPTS is more efficient to stabilize small size of PdNPs-HCOONa. In addition, the above four samples were further subjected to ICP-MS analysis after dialyze; and found that in all the cases, >95% palladium precursor was converted to palladium nanoparticles(Table S1).

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Figure 2. TEM image of PdNPs catalyst originated from various reductants. A) NH_2NH_2 , the size of PdNPs was about 8.7 nm; B) $NaBH_4$, the size of PdNPs was mainly distributed between 2.1-4.9 nm; C) ascorbic acid, the size of PdNPs was around 2.5 nm; D) HCOONa, the size of PdNPs was about 1.5 nm with a narrow distribution.

Next, these PdNPs were subjected to Suzuki-Miyaura reaction for evaluating their catalysis activity. The PdNPs was used directly for catalysis without a dialyze process. Phenylboronic acid and 4-bromoanisole were selected as model substrates, the amount of PdNPs was set as 0.01mol% (according to 4bromoanisole). The reaction was performed in the 50% ethanol aqueous solution at room temperature for 0.5 h. The conversion are listed in table 1. These nanopartciels showed varied performances for the reactions. PdNPs-NH2NH2 showed nearly no catalytic activity and only 2% conversion after 30 min was achieved (table 1, entry 1). PdNPs-NaBH4 and PdNPs-Vc offered only 8% and 12% conversion, respectively (entry 2 and 3). The best conversion was achieved when PdNPs-HCOONa was used as catalyst, which was 95% (entry 4). These results indicated that the catalysis activity was depended on the size of palladium nanoparticles, the small size of nanoparticle PdNPs-HCOONa give the higher activity.

Table 1

Screening of catalysis activity under various reaction conditions^a

MeO—	Br + (HO)₂B→	EtOH/H2O	MeO
Entry	Reducing agent	Capping agent	Yield ^b
1	NH_2NH_2	TPPTS	2%
2	$NaBH_4$	TPPTS	8%
3	Ascorbic acid	TPPTS	12 %
4	HCOONa	TPPTS	95%
5	-	TPPTS	20%
6	HCOONa	-	8%
7	HCOONa	PVP	1%

^a Reaction condition: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), K_3PO_4 (1mmol), 0.01 mol% of PdNPs (according to 4-bromoanisole), the reaction was carried out in 50% ethanol aqueous solution at room temperature nitrogen.

^b isolated yield.

The scope of substrate was further investigated, as shown in Table 2. The electron donating substituted aromatic bromides could be preceded smoothly and high yield of biaryl product was gained within 2 h at room temperature (table 2, entry 1-4). PdNPs-HCOONa were also high activity in catalyzing the electron withdrawing aromatic bromides at room temperature and >98% yield was gained for 4nitrobromobenzene or ethyl 4-bromobenzoate as substrate in 4 h (entry 5 and 6). 2-bromonaphthalene is nearly full conversion to 2-phenylnaphthalene within 1 h (entry 7). In addition, the catalysis activity of PdNPs-HCOONa for substituted arylboronic acid was also investigated, and found that reaction was also underway smoothly with 1naphthylboronic acid and 4-methoxyphenylboronic acid as substrates (entry8-10).

Table 2

Suzuki coupling of aryl halides and ArB(OH)2^a

$R_1 \longrightarrow Br + (HO)_2 B \longrightarrow R_2 \xrightarrow{HPP1SPd} MeO \longrightarrow MeO$						
Entry	Aryl halide	ArB(OH) ₂	Time (h)	Yield ^b		
1	Br	(HO) ₂ B	1	97%		
2	Br	(HO) ₂ B	1	98%		
3	HO-Br	(HO) ₂ B	1	99%		
4	Br	(HO) ₂ B	1	97%		
5	O ₂ N-Br	(HO) ₂ B	2	98%		
6	EtOOC Br	(HO) ₂ B	2	99%		
7	Br	(HO) ₂ B	1	98%		
8	MeO-Br	B(OH) ₂	1	97%		
9	MeO	B(OH) ₂	1	98%		
10	MeO-Br	(HO) ₂ B-OMe	1	99%		

^a Aryl halides (0.5 mmol), $ArB(OH)_2$ (0.75 mmol), K_3PO_4 (1mmol), 0.01 mol% of PdNPs-HCOONa (according to aryl halides), the reaction was performed out in 50% ethanol aqueous solution at room temperature under nitrogen.

^b isolated yield.

For further investigation on the effectiveness of TPPTS in this catalysis system, the following control experiments were performed by using the 4-bromoanisole and phenylboronic acid as model substrates. First, instead of using PdNPs, K_2PdCl_4 was directly added to the reaction solution together with TPPTS, and only 20% conversion was achieved (table1, entry5). Second, K_2PdCl_4 was reduced into PdNPs by HCOONa but without the TPPTS as the capping agent. In this case, only 8% conversion was gained (table1, entry6). Third, TPPTS was replaced by PVP as the stabilizer for the PdNPs. In this condition, only trace product was obtained (table1, entry7), in spite of the TEM images proved the size of PdNPs was as small as 2.3 nm (Fig. S1). These results proved that in this catalysis system, the

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catalytic activity was improved significantly when converting palladium precursor K_2PdCl_4 to PdNPs. Moreover, in comparing with naked PdNPs or PVP coated PdNPs, the modification of TPPTS on PdNPs enhanced the catalytic activity significantly.

According the above experiment results, we proposed the following explanation: the catalytic activity of PdNPs-HCOONa is decided by the following two aspects; one is the size of nanoparticles is small enough to contribute more surface atoms; another key point is the surface of nanoparticles should be covered by TPPTS, which could stable the nanoparticles and also further activated the surface palladium atoms; that is, the catalytic specious in our case should be the TPPTS coordinated surface atoms on the palladium nanoparticles.

Conclusion

In summary, a water dispersible PdNPs with TPPTS as stabilizer was developed. The resulted PdNPs can catalyse the Suzuki-Miyaura reaction in aqueous media. The catalytic activity was depended on the size of PdNPs and the smallest PdNPs reduced by HCOONa gives the highest catalytic activity. TPPTS acted not only as a stabilizer, but also an activator for PdNPs. This work provided a new insight into the design concept of the green nanocatalyst, water dispersible and size control.

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Highlights

TPPTS capped palladium nanoparticles catalyzed Suzuki-Miyaura coupling efficiently.

The reaction was performed under the mild condition.