Catal Lett (2013) 143:578–586
DOI 10.1007/s10562-013-0989-3

G-/C-rich Oligonucleotides Stabilized Pd Nanocatalysts for the Suzuki Coupling Reaction Under Mild Conditions

Wei Li · Yingming Fu · Yan Fu · Xian Wang · Jinli Zhang

Received: 24 January 2013 / Accepted: 3 March 2013 / Published online: 13 March 2013

Abstract Pd nanoparticles with narrow size distributions between 1.3 and 3.3 nm are prepared using G-/C-rich oligonucleotide as the template. These DNA-Pd nanoparticles efficiently catalyze the Suzuki coupling reaction and exhibit highly catalytic activities under mild conditions, which are greatly dependent upon the particle size of Pd nanoparticles besides the DNA sequence. For the coupling reaction of iodobenzene and phenylboronic acid at 60 °C in the presence of KOH, it can be achieved high TOF value of 2646 mol biphenyl (mol Pd × h)$^{-1}$ over AG22-Pd and 3640 mol biphenyl (mol Pd × h)$^{-1}$ over CT22-Pd. Under the optimal experimental conditions, the yield of 100 % in biphenyl is obtained with only 0.0055 mol% AG22-Pd at 60 °C for 1 h in the solvent of EtOH/H_2O (1:2) using Na_2CO_3 or K_2CO_3 as the base. It is illustrated that G-/C-rich oligonucleotides are promising templates to modulate easily the morphology of Pd nanoparticles in aqueous solution with high catalytic activity.

Keywords DNA · Palladium nanoparticles · Suzuki cross-coupling

1 Introduction

Suzuki cross-coupling reaction, one of the most widely used protocols for the formation of carbon–carbon bonds, has presented wide applications in the production of polymers, agrochemicals, pharmaceutical intermediates and high-tech materials [1, 2], which are generally catalyzed by soluble palladium complexes with various ligands such as phosphines, N-heterocyclic carbenes [3]. Owing to high surface-to-volume ratio and highly active surface atoms, palladium nanoparticles (Pd NPs) catalyzed Suzuki cross-coupling reactions have been extensively studied recently [1, 2, 4], indicating that a critical nanoparticle size exist in the Suzuki cross-coupling reaction with high catalytic activities while small clusters were found to be less catalytically active. El-Sayed and co-workers investigated the catalytic activity of different-sized poly(vinylpyrrolidone)-capped Pd nanoparticles in Suzuki cross-coupling between iodobenzene and phenylboronic acid at 80 °C in the solvent of CH_3CN/H_2O (3:1) using NaOAc as the base, and showed that Pd NPs with a particle size of 4–5 nm exhibit the highest turnover frequency (TOF) [5, 6]. Therefore, the controllable synthesis of Pd NPs with tunable and uniform size play a critical role for the design of efficient catalysts in these important reactions. On the other hand, compared with Pd nanocatalysts based on conventional supports involving silica [7], metal oxide [8, 9], carbon nanotube [10, 11], and polymeric microsphere [12], Pd NPs stabilized by dendrimer [13, 14], cyclodextrin [15], peptide [16–18], etc., have attracted much attention in C–C coupling reactions owing to the advantage of conveniently controlling the shape and size distribution of particles. For example, Knecht and coworkers reported that peptide selected by phage display has the ability to finely tune the size, surface structure and functionality of single-crystal Pd

Electronic supplementary material The online version of this article (doi:10.1007/s10562-013-0989-3) contains supplementary material, which is available to authorized users.

W. Li (✉) · Y. Fu · Y. Fu · X. Wang · J. Zhang
Key Laboratory of Systems Bioengineering MOE, Key Laboratory for Green Chemical Technology MOE, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, People's Republic of China
e-mail: liwei@tju.edu.cn

NPs between 1.9 and 3.1 nm, and the peptide-Pd NPs with the critical particle size exhibit high reactivity in Stille coupling reaction [19]. Therefore, exploration of novel polymer stabilizer to control the particle size is promising for enhancing the catalytic activities in C–C coupling reactions as well as achieving more environmental-benign synthetic processes.

Nucleic acids, which enrich nitrogen and oxygen functional groups that coordinate with metallic nanoparticles, have emerged as promising biotemplates for the construction of nanomaterials [20–22]. A number of reports suggested that the sequence composition of nucleic acids can greatly influence morphologies [23, 24] or electric properties [25, 26] of palladium nanomaterials. Considering green and sustainable organic synthesis, natural DNA molecules extracted from salmon sperm or calf thymus with low toxicity have been performed as a catalytic support to control the dispersibility of Pd NPs, which has been successfully assessed in a series of organic reactions involving oxidation, reduction or C–C cross-coupling [27]. For instance, Pd NPs templated by salmon DNA with a distribution of 5–8 nm were found to be effective in the Suzuki reaction between aryl halides and phenylboronic acid, i.e., 4-nitrophenyl iodide was produced in a high yield of 93 % at 60 °C for 48 h using Na_2CO_3 as the base [28]. Furthermore, the yield in the reaction between phenylboronic acid and iodobenzene can reach as high as 100 % at 100 °C for 4 min catalyzed by ctDNA-capping Pd NPs on graphene in the range of 4–6 nm [29]. Electron-rich nitrogen atoms in DNA bases especially N1, N7 sites of guanine (G) and N3 site of cytosine (C), provide active sites coordinating with transition metal ions including Ag^+, Pt^{2+}, Pd^{2+} [30]. G-/C-rich oligonucleotides have been reported to synthesize silver nanoclusters and regulate their fluorescent properties [31–33]. However, few reports focus on the synthesis of Pd NPs using G-/C-rich oligonucleotide as the template to modulate the catalytic characteristics in organic reactions such as Suzuki cross-coupling.

In the present study, G-rich oligonucleotide d[$AG_3(T_2AG_3)_3$] and C-rich d[$(C_3TA_2)_3C_3T$] are used as the templates to synthesize monodispered Pd NPs. These DNA-Pd NPs exhibit highly catalytic activities in the Suzuki coupling reactions in aqueous solution, which are greatly dependent upon the particle size of Pd NPs. Effects of reaction solvents, base species and different types of aryl halides are studied in order to optimize the catalytic performance of DNA-templated Pd NPs under mild conditions. It is illustrated that G-/C-rich oligonucleotides are promising templates to modulate easily Pd NPs with high catalytic activity. The yield of 100 % in biphenyl is obtained with only 0.0055 mol% AG22-Pd at 60 °C for 1 h in the solvent of EtOH/H_2O (1:2) using Na_2CO_3 or K_2CO_3 as the base, while the production of 4-phenylbenzoic acid gives the highest yield with 0.11 mol% AG22-Pd in the presence of NaOH.

2 Experimental

2.1 Chemicals

Oligonucleotides d[$AG_3(T_2AG_3)_3$] and d[$(C_3TA_2)_3C_3T$] (denoted as AG22 and CT22 respectively) were purchased from Japanese Takara Bio (Dalian) with the purity higher than 98 % measured by high performance liquid chromatography (HPLC). Na_2PdCl_4 (99.95 %), 4-iodobenzoic acid (97 %) and 4-phenylbenzoic acid (98 %) were purchased from Alfa Aesar. $NaBH_4$ (98 %), sodium acetate trihydrate (99 %), K_2CO_3 (99 %), Cs_2CO_3 (99.5 %), KOH (82 %), iodobenzene (98.5 %), bromobenzene (98.5 %), chlorobenzene (99.0 %), 4-chlorobenzoic acid (99.5 %) and dimethylformamide (DMF, 99.5 %) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Glacial acetic acid (99.5 %), Na_2CO_3 (99.8 %), NaOH (96 %) and ethanol (EtOH, 99.7 %) were purchased from Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd. $K_3PO_4{\cdot}3H_2O$ (99 %), 4-bromobenzene acid (99 %) and N-methyl pyrrolidone (NMP, 98 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. Phenylboronic acid was purchased from TCI Shanghai. Biphenyl (99.5 %) was purchased from J&K Scientific Ltd. Acetonitrile (CH_3CN, 99.9 %) was purchased from Merck KgaA. N,N-dimethyl acetamide (DMAC, 99.5 %) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All reagents were used as received without purification.

2.2 Characterizations

UV spectroscopy were recorded on a Cary-300 Bio UV–Visible spectrophotometer (Varian Ltd.) using a 1 mm path quartz cuvette at 25 °C. Transmission Electron Microscopy (TEM) were performed on JEM-2010FEF equipment (JEOL, Japan). Electron microscopy samples were prepared by applying 10 μL samples on a carbon-coated grid for 10 min, and then excess liquid was removed with filter paper. HPLC was carried out at ambient temperature on a Agilent 1200 system equipped with a UV detector. Analysis of the products of Suzuki coupling reaction was performed on a Agilent Eclipse XDB-C18 column (5 μm, 150 × 4.6 mm). The product of biphenyl was analyzed using acetonitrile/water mixture (60/40, v/v) as mobile phase at a flow rate of 1 mL/min at the detection wavelength of 254 nm and the product of 4-phenylbenzoic acid was detected using acetonitrile/glacial acetic acid (0.1 %) mixture (40/60, v/v) as mobile phase at the detection wavelength of 270 nm. Quantitative analysis was calculated by using external standard method.

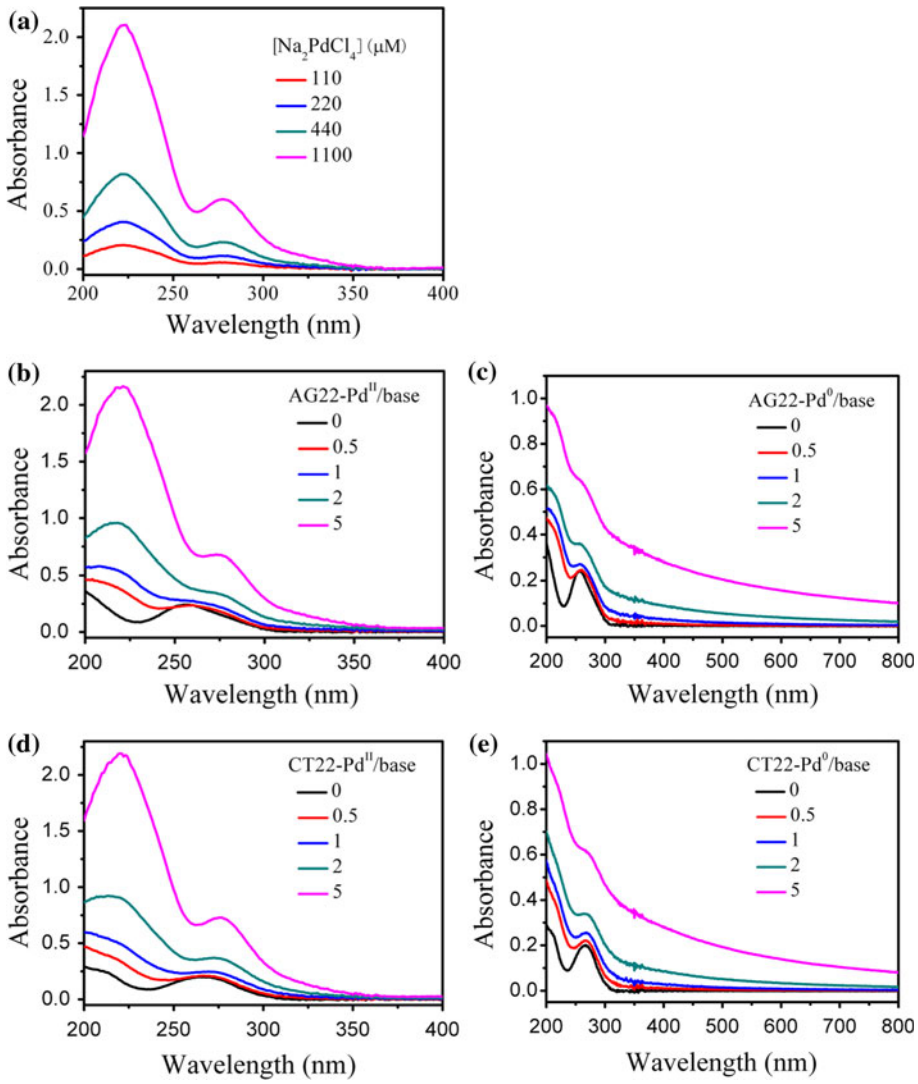


Fig. 1 UV–Vis spectra of the Na_2PdCl_4 in the absence of DNA (**a**). UV–Vis spectra of the AG22-Pd^{II} complexes (**b**) and AG22-Pd^0 after reduction with $NaBH_4$ at different Pd/base ratios (**c**). UV–Vis spectra of the CT22-Pd^{II} complexes (**d**) and CT22-Pd^0 after reduction with $NaBH_4$ at different Pd/base ratios (**e**)

2.3 Preparation and Catalytic Performance of DNA-templated Pd NPs

Oligonucleotide AG22 and CT22 were chosen as the template to synthesize Pd NPs in 10 mM KH_2PO_4–K_2HPO_4 potassium phosphate buffer (10 mM, pH 5.0) and they were carried out in open air. All DNA samples were annealed by heating the sample cuvette to 95 °C for 5 min and then cooling to 4 °C. The Pd NPs were synthesized through reduction of Na_2PdCl_4 by BH_4^-. Oligonucleotides dissolved in KH_2PO_4–K_2HPO_4 buffer were firstly incubated with Na_2PdCl_4 at Pd/base ratio of 0.5, 1, 2, 5 for 0.5 h, and then adding $NaBH_4$ (2 equiv) to Na_2PdCl_4 to start the reduction reaction for 0.5 h.

2.4 Suzuki Coupling Reaction

All the reactions were carried out in a 10 mL ground glass stoppered flask containing 0.1 mmol aryl halide, 0.125 mmol phenylboronic acid and 0.25 mmol base in the presence of a certain amount of DNA-Pd catalyst in 2 mL solvent. After stirring at 60 °C for 1 h, the reaction mixture was cooled in a water–ice bath to stop the reaction, and then 6 mL of acetonitrile–water mixture was added to dissolve the reaction mixture. The product diluted with mobile phase was analyzed with the HPLC.

3 Results and Discussion

3.1 Preparation and Characterization of Oligonucleotide-Capping Pd NPs

As shown in the UV–Vis spectra of the AG22-Pd^{II} complexes (Fig. 1b), a ligand-to-metal charge-transfer (LMCT) band is observed around 215 nm for the AG22-Pd^{II} prior to reduction, which contributes to the interaction of Pd^{II} ions with nitrogen atoms in guanine bases [34]. As the Pd/base

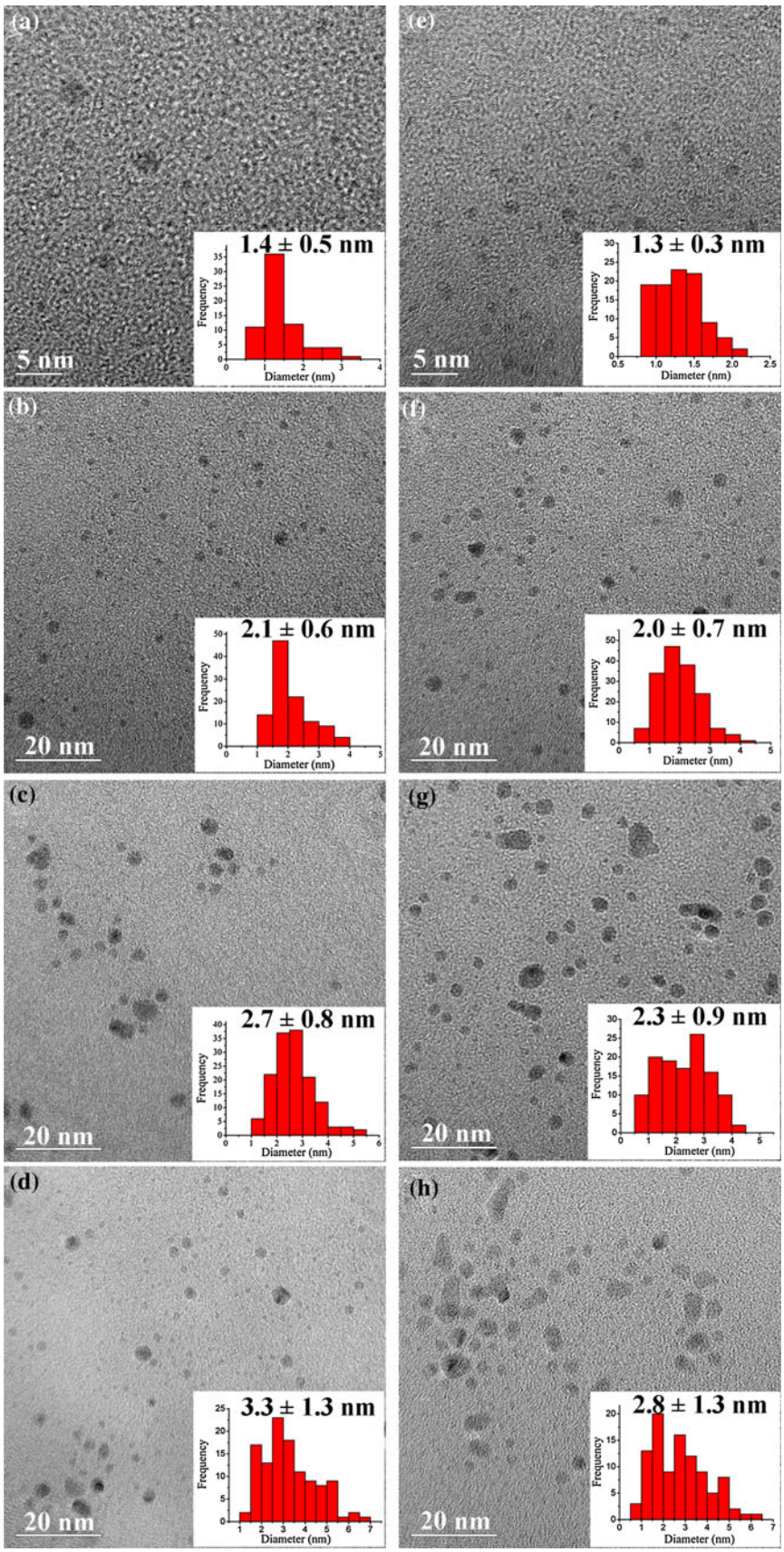


Fig. 2 TEM images of Pd nanoparticles templated by AG22 at Pd/base ratio of 0.5 (**a**), 1 (**b**), 2 (**c**), 5 (**d**), as well as Pd NPs templated by CT22 at Pd/base ratio of 0.5 (**e**), 1 (**f**), 2 (**g**), 5 (**h**)

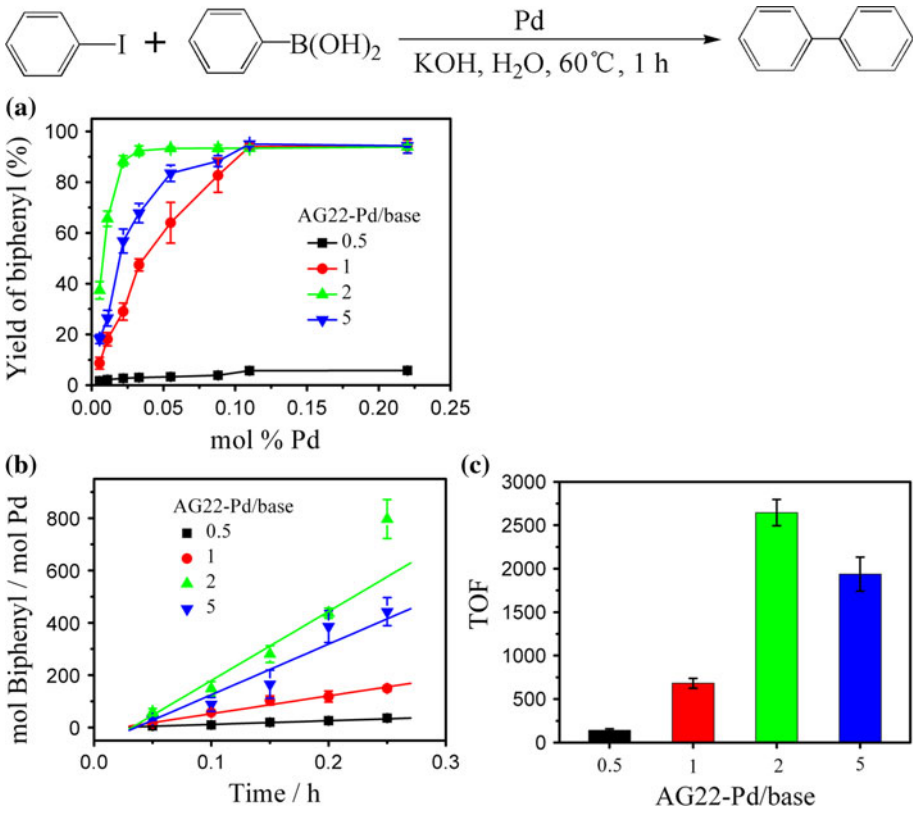


Fig. 3 **a** The yield of biphenyl with AG22-Pd NPs loadings of 0.0055–0.22 mol% at different Pd/base ratios, yield = (moles of biphenyl)/(moles of iodobenzene) × 100 %; **b** TOF analysis of AG22-Pd NPs prepared at Pd/base ratio of 0.5, 1, 2, 5 respectively, the yields of biphenyl at different reaction times (3 min, 6 min, 9 min, 12 min or 15 min) are plotted as the mol biphenyl/mol Pd, and the slope derived from linear fitting represents the TOF value; **c** TOF comparison of four AG22-Pd NPs (y-axis units = mol biphenyl (mol Pd × h)$^{-1}$), a catalyst loading of 0.033 mol% is employed in TOF determination

ratio increasing, the intensity of the LMCT band also increases; however, a slight red-shift to 220 nm is observed at the Pd/base ratio of 5 due to the free Pd^{II} ions in solution (Fig. 1a). After reduction of the DNA-Pd^{II} complex, the LMCT band disappears and a broad absorbance band appears in this region, indicating that Pd^{II} are reduce into Pd^0 NPs (Fig. 1c). Similar spectral changes are also observed for the synthesis of Pd NPs templated by C-rich oligonucleotide (Fig. 1d, e).

Adopting the oligonucleotide AG22 (Fig. 2a–d), the average size gradually increases from 1.4 nm to 3.3 nm with the Pd/base ratio ranging from 0.5 to 5. Moreover, CT22-Pd NPs show smaller particle size ranging from 1.3 nm to 2.8 nm at the same Pd/base ratio (Fig. 2e–h). Compared with the polynucleotide template of natural fish sperm DNA, which prepared Pd nanohybrids with an average diameter of 7–8 nm [27], it is indicated that G-/C-rich oligonucleotides are superior to control efficiently and easily the size contribution of Pd NPs.

3.2 Suzuki Reactions in Aqueous Medium Catalyzed by DNA-Pd NPs

Suzuki reactions of iodobenzene and phenylboronic acid to produce biphenyl are firstly performed using AG22-Pd NPs with different particle size (illustrated in Fig. 2a–d). As shown in Fig. 3a, the catalytic activities of the Pd NPs increasing significantly with the Pd/base ratio of 0.5–2, i.e., the product yield can reach to 92.4 % with only 0.033 mol% Pd using the AG22-Pd NPs of 2.7 nm (Pd/base = 2). However, the catalytic activity decreases with the Pd NPs of 3.3 nm, suggesting a critical particle size of 2.7 nm for the Pd NPs templated by G-rich AG22 in the Suzuki coupling. Furthermore, the highest TOF value of 2646 ± 152 mol biphenyl (mol of Pd × h)$^{-1}$ is achieved at Pd/base of 2 with the average size of 2.7 nm (Fig. 3b, c). These results suggest that the smallest particle size can not result in an increased reaction rate in the Suzuki reaction. Most of Pd^{II} anticipates in the coordination with nitrogen atoms in DNA bases at the ratio of 0.5, thus, the sample is most difficult to reduce and less reactive Pd^0 is presented. As the part of DNA coordinating Pd^{II} decreases with increasing the Pd/base ratio, more Pd^{II} is reduced to active Pd^0 to generate high TOFs [34]. Therefore, it is clear that there is a balance between the protection of Pd NPs against further agglomeration and either the Pd leaching or the free access for the reactants to the PdNP surface. Similarly, the catalytic activities of PVP-stabilized Pd NPs have been reported to decrease in the order of Pd (3.9 nm) > Pd (3.0 nm) ≈ Pd (5.2 nm) > Pd (6.6 nm) on the Suzuki reaction between phenylboronic acid and iodobenzene [5].

In the case of C-rich oligonucleotide CT22, the TOF value of 3640 mol biphenyl (mol Pd × h)$^{-1}$ can be achieved at the Pd/base ratio of 2 under similar conditions

Table 1 Effect of solvent on the Suzuki reaction between aryl halide and phenylboronic acid catalyzed by AG22-Pd NPs

Entry	R	Solvent (v/v)	Pd (mol%)	Yield (%)
1	H	H_2O	0.033	92.4
2	H	EtOH/H_2O = 1:2	0.033	100
3	H	EtOH/H_2O = 1:1	0.033	100
4	H	CH_3CN/H_2O = 1:2	0.033	9.8
5	H	CH_3CN/H_2O = 1:1	0.033	2.9
6	H	DMF/H_2O = 1:2	0.033	0.3
7	H	DMF/H_2O = 1:1	0.033	0.2
8	H	NMP/H_2O = 1:2	0.033	2.3
9	H	NMP/H_2O = 1:1	0.033	0.4
10	H	DMAC/H_2O = 1:2	0.033	10.9
11	H	DMAC/H_2O = 1:1	0.033	2.5
12	COOH	H_2O	0.11	92.7
13	COOH	EtOH/H_2O = 1:2	0.11	96.9
14	COOH	EtOH/H_2O = 1:1	0.11	96.5
15	COOH	CH_3CN/H_2O = 1:2	0.11	72.8
16	COOH	CH_3CN/H_2O = 1:1	0.11	74.5
17	COOH	DMF/H_2O = 1:2	0.11	0.5
18	COOH	DMF/H_2O = 1:1	0.11	0.4
19	COOH	NMP/H_2O = 1:2	0.11	70.1
20	COOH	NMP/H_2O = 1:1	0.11	29.2
21	COOH	DMAC/H_2O = 1:2	0.11	71.1
22	COOH	DMAC/H_2O = 1:1	0.11	48.7

Reaction conditions: aryl halide (0.1 mmol, 1 equiv), PhB(OH)2 (0.125 mmol, 1.25 equiv), KOH (0.25 mmol, 2.5 equiv), solvent (2 mL), 60 °C, 1 h. AG22-Pd NPs (Pd/base = 2) was used here as the catalyst. Each sample was repeated at least three times

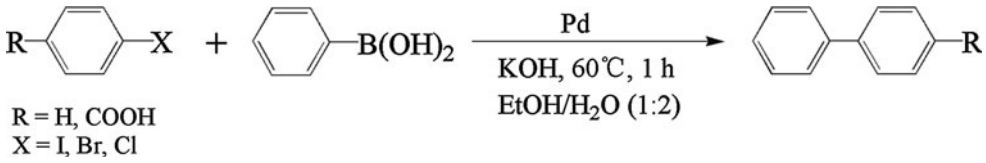
(Fig. S1c). Therefore, it is suggested that the critical particle size is around 2.7 nm for AG22-Pd while 2.3 nm for CT22-Pd both at the Pd/base of 2.

3.3 Optimization of Catalytic Activities of DNA-Pd NPs in Suzuki Coupling Reactions

Effects of reaction solvents, base species and different types of aryl halides are studied in order to optimize the catalytic performance of DNA-templated Pd NPs under mild conditions. Firstly, we attempt to use the mixtures of water with a series of organic solvents as the reaction medium to improve the solubility of the initial reactants. As listed in Table 1, the yield of 100 % for biphenyl at 0.033 mol% Pd with AG22-Pd NPs synthesized at Pd/base of 2 is produced in the 1:2 and 1:1 mixture of EtOH/H_2O (v/v). In contrast, these water-soluble DNA-Pd NPs are not compatible with other organic solvents including CH_3CN, DMF, NMP, or DMAC, which might cause changes to the particle surface to alter the specific interactions that drive the chemical reactions [35]. Similarly, the yield of 96.9 % for 4-phenylbenzoic acid at 0.11 mol% Pd can be achieved in the 1:2 mixture of EtOH/H_2O, and other solvents in the reaction system also inhibit the catalytic activities.

Next, in order to study the reactivities and specificities of DNA-Pd NPs, Suzuki reactions of various aryl halide with phenylboronic acid are carried out as shown in Table 2. Substitution of the halide for bromide or chloride functionalities result in a decrease in reactivity, i.e., the yield of biphenyl decreases to 87.9 % for bromobenzene while 1.6 % for chlorobenzene even with high catalyst loading of 0.033 mol% Pd. These results are well consistent with previous studies on the Stille C–C coupling reactions using peptide stabilized Pd NPs (1.9 nm) due to the lesser activity of the lighter halides [35]. In the case of 4-halobenzoic acids, substitution of the halide similarly resulted in decreased reaction yields. A significant decrease in the yield of 4-phenylbenzoic acid is also observed especially for the substitution of the halide for chloride.

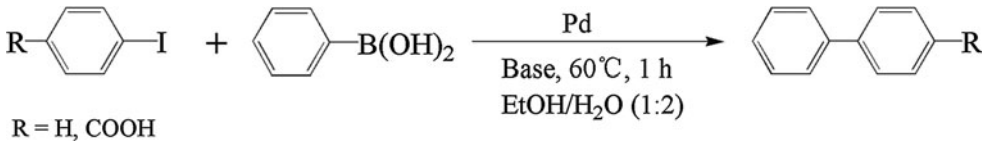
Table 2 The coupling reactions between various aryl halides and phenylboronic acid catalyzed by AG22-Pd NPs



Entry	R	X	Pd (mol%)	Yield (%)
1	H	I	0.0088	100
2	H	Br	0.033	87.9
3	H	Cl	0.033	1.6
4	COOH	I	0.088	94.9
5	COOH	I	0.11	96.9
6	COOH	Br	0.11	94.7
7	COOH	Cl	0.11	2.3

Reaction conditions: aryl halide (0.1 mmol, 1 equiv), PhB(OH)2 (0.125 mmol, 1.25 equiv), KOH (0.25 mmol, 2.5 equiv), EtOH/H2O (2 mL, v/v = 1:2), 60 °C, 1 h. The AG22-Pd NPs (Pd/base = 2) was used here as the catalyst. Each sample was repeated at least three times

Table 3 Effect of various bases on the Suzuki reaction between aryl halide and phenylboronic acid catalyzed by AG22-Pd NPs



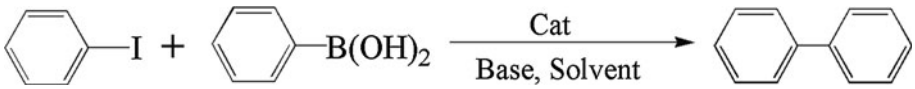
Entry	R	Base	Pd (mol%)	Yield (%)
1	H	NaOAc	0.033	1.7
2	H	Na_2CO_3	0.0022	92.3
3	H	Na_2CO_3	0.0055	100
4	H	K_2CO_3	0.0022	89.0
5	H	K_2CO_3	0.0055	100
6	H	NaOH	0.0022	69.8
7	H	NaOH	0.0055	92.9
8	H	NaOH	0.0088	100
9	H	KOH	0.0022	42.0
10	H	KOH	0.0055	87.7
11	H	KOH	0.0088	100
12	COOH	NaOAc	0.11	1.1
13	COOH	Na_2CO_3	0.11	97.0
14	COOH	K_2CO_3	0.11	86.6
15	COOH	NaOH	0.11	99.8
16	COOH	KOH	0.11	96.9

Reaction conditions: aryl halide (0.1 mmol, 1 equiv), PhB(OH)2 (0.125 mmol, 1.25 equiv), Base (0.25 mmol, 2.5 equiv), EtOH/H2O (2 mL, v/v = 1:2), 60 °C, 1 h. The AG22-Pd NPs (Pd/base = 2) was used here as the catalyst. Each sample was repeated at least three times

Finally, a series of bases involving NaOAc, Na_2CO_3, K_2CO_3, NaOH, and KOH, are investigated to enhance the catalytic performance in the Suzuki coupling reactions (Table 3). For the reaction of iodobenzene and phenylboronic acid, the yield of biphenyl can reach to 100 % with the catalyst loading of 0.0055 % in the presence of Na_2CO_3 and K_2CO_3, while the yield of 100 % is obtained with 0.0088 % mol Pd NPs in the presence of NaOH and KOH. For the reaction of 4-iodobenzoic acid and phenylboronic acid, the highest product yield (99.8 %) occurs in the presence of NaOH, and the yields decrease with the bases in the following order: NaOH > KOH $\approx$ Na_2CO_3 > K_2CO_3 > NaOAc.

As shown in Table 4, compared with the other four Pd catalysts, DNA-Pd nanocatalyst used in this study exhibit

Table 4 Suzuki reaction of iodobenzene with phenylboronic acid via different Pd catalysts



Entry	Catalyst (mean diameter)	Pd loading (mol%)	Solvent	Base	Temp (°C)	Time (h)	Yield (%)
1	AG22-Pd (2.7 nm)	0.0055	EtOH/H_2O (1:2, v/v)	Na_2CO_3	60	1	100
2	PVP-Pd [36] (3.6 nm)	0.3	EtOH/H_2O (2:3, v/v)	Na_3PO_4	Reflux	12	95
3	G3-OHdendrimer-Pd [37] (1.4 nm)	1.5	EtOH/H_2O (2:3, v/v)	Na_3PO_4	Reflux	24	71
4	α-HPCD-Pd [15] (3.7 nm)	0.01	H_2O	K_2CO_3	60	24	100
5	PNIPAM-Pd [38] (3 nm)	0.2	H_2O	K_2CO_3	90	5	99

high efficiency for the Suzuki reaction between iodobenzene and phenylboronic acid under mild conditions. For example, the yield of 95 % in biphenyl was obtained with 0.3 mol% PVP-Pd NPs (3.6 nm) at reflux for 12 h in the 2:3 mixture of EtOH/H_2O using Na_3PO_4 as the base [36]. Moreover, in the case of α-HPCD-Pd NPs of 3.7 nm, the yield of biphenyl reaches to 100 % with 0.01 mol% Pd loading at 60 °C for 24 h in H_2O using K_2CO_3 as the base [15]. In this study, the yield of 100 % in biphenyl is obtained with only 0.0055 mol% AG22-Pd at 60 °C for 1 h in the 1:2 mixture of EtOH/H_2O using Na_2CO_3 or K_2CO_3. Considering facile synthesis and high catalytic activity, oligonucleotide-Pd nanocatalysts likely to be a promising alternative.

4 Conclusions

Pd NPs are successfully synthesized in aqueous solution using G-/C-rich oligonucleotide as an efficient stabilizer. Pd NPs with the average particle size from 1.4 nm to 3.3 nm are produced by the reduction of Pd^{II} in the presence of G-rich template at the Pd^{II}/base ratio of 0.5–5, while Pd NPs ranging from 1.3 nm to 2.8 nm can be generated by C-rich template under similar conditions. These DNA-Pd NPs exhibit highly catalytic activities in the Suzuki coupling reactions under mild conditions, which are greatly dependent upon the particle size of Pd NPs. The critical particle size is found to be 2.7 nm for AG22-Pd while 2.3 nm for CT22-Pd at the Pd^{II}/base of 2. For the coupling reaction of iodobenzene and phenylboronic acid at 60 °C in the presence of KOH, it can be achieved high TOF value of 2646 mol biphenyl (mol Pd × h)$^{-1}$ over AG22-Pd and 3640 mol biphenyl (mol Pd × h)$^{-1}$ over CT22-Pd. Under the optimal reaction conditions, the yield of 100 % in biphenyl is obtained with only 0.0055 mol% AG22-Pd at 60 °C for 1 h in the solvent of EtOH/H_2O (1:2) using Na_2CO_3 or K_2CO_3 as the base, while the production of 4-phenylbenzoic acid gives the highest yield with 0.11 mol% AG22-Pd in the presence of NaOH. It is illustrated that G-/C-rich oligonucleotides are promising templates to modulate easily the morphology of Pd NPs in aqueous solution with high catalytic activity.

Acknowledgments This work was supported by NSFC (21276179, 20836005), and the Special Funds for Major State Basic Research Program of China (2012CB720300).

References

1. Fihri A, Bouhrara M, Nekoueishahraki B, Basset JM, Polshettiwar V (2011) Chem Soc Rev 40:5181
2. Perez-Lorenzo M (2012) J Phys Chem Lett 3:167
3. Li HB, Seechurn CCCJ, Colacot TJ (2012) ACS Catal 2:1147
4. Balanta A, Godard C, Claver C (2011) Chem Soc Rev 40:4973
5. Li Y, Boone E, El-Sayed MA (2002) Langmuir 18:4921
6. Narayanan R, Tabor C, El-Sayed MA (2008) Top Catal 48:60
7. Kim M, Heo E, Kim A, Park JC, Song H, Park KH (2012) Catal Lett 142:588
8. Kantam ML, Roy S, Roy M, Sreedhar B, Choudary BM (2005) Adv Synth Catal 347:2002
9. Monopoli A, Nacci A, Calo V, Ciminale F, Cotugno P, Mangone A, Giannossa LC, Azzone P, Cioffi N (2010) Molecules 15:4511
10. Corma A, Garcia H, Leyva A (2005) J Mol Catal A Chem 230:97
11. Zhang PP, Zhang XX, Sun HX, Liu RH, Wang B, Lin YH (2009) Tetrahedron Lett 50:4455
12. Ohtaka A, Kono Y, Teratani T, Fujii S, Matsuzawa S, Nakamura Y, Nomura R (2011) Catal Lett 141:1097
13. Diallo AK, Ornelas C, Salmon L, Aranzaes JR, Astruc D (2007) Angew Chem Int Ed 46:8644
14. Ornelas C, Ruiz J, Salmon L, Astruc D (2008) Adv Synth Catal 350:837
15. Senra JD, Malta LFB, da Costa MEHM, Michel RC, Aguiar LCS, Simas ABC, Antunes OAC (2009) Adv Synth Catal 351:2411
16. Coppage R, Slocik JM, Sethi M, Pacardo DB, Naik RR, Knecht MR (2010) Angew Chem Int Ed 122:3855
17. Jakhmola A, Bhandari R, Pacardo DB, Knecht MR (2010) J Mater Chem 20:1522
18. Briggs BD, Knecht MR (2012) J Phys Chem Lett 3:405
19. Coppage R, Slocik JM, Briggs BD, Frenkel AI, Naik RR, Knecht MR (2012) ACS Nano 6:1625
20. Berti L, Burley GA (2008) Nat Nanotechnol 3:81
21. Ma N, Tikhomirov G, Kelley SO (2009) Acc Chem Res 43:173
22. Diez I, Ras RHA (2011) Nanoscale 3:1963
23. Gugliotti LA, Feldheim DL, Eaton BE (2004) Science 304:850
24. Gugliotti LA, Feldheim DL, Eaton BE (2005) J Am Chem Soc 127:17814

25. Richter J, Mertig M, Pompe W, Monch I, Schackert HK (2001) Appl Phys Lett 78:536
26. Mertig M, Seidel R, Ciacchi LC, Pompe W (2002) In: Kuzmany H, Fink J, Mehring M, Roth S (eds) Structural and electronic properties of molecular nanostructures, vol. 633. The American Institute of Physics, Melville
27. Wang Y, Ouyang GH, Zhang JT, Wang ZY (2010) Chem Commun 46:7912
28. Itoh H, Maeda H, Yamada S, Hori Y (2012) ChemCatChem 4:1737
29. Qu KG, Wu L, Ren JS, Qu XG (2012) ACS Appl Mater Interfaces 4:5001
30. Rombeck I, Lippert B (1998) Inorg Chim Acta 273:31
31. Zheng L, Zhang RC, Ni YX, Du QA, Wang X, Zhang JL, Li W (2010) Catal Lett 139:145
32. Fu Y, Zhang JL, Chen XF, Huang TT, Duan XL, Li W, Wang JK (2011) J Phys Chem C 115:10370
33. Wu JJX, Fu Y, He ZH, Han Y, Zheng L, Zhang JL, Li W (2012) J Phys Chem B 116:1655
34. Coppage R, Slocik JM, Briggs BD, Frenkel AI, Heinz H, Naik RR, Knecht MR (2011) J Am Chem Soc 133:12346
35. Pacardo DB, Sethi M, Jones SE, Naik RR, Knecht MR (2009) ACS Nano 3:1288
36. Li Y, Hong XM, Collard DM, El-Sayed MA (2000) Org Lett 2:2385
37. Li Y, El-Sayed MA (2001) J Phys Chem B 105:8938
38. Wei GW, Zhang WQ, Wen F, Wang Y, Zhang MC (2008) J Phys Chem C 112:10827