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Size controlled synthesis of Pd nanoparticles in water and their catalytic application in C–C coupling reactions

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ABSTRACT

Catalytically active Pd nanoparticles have been synthesized in water by a novel reduction of Pd(II) with a Fischer carbene complex where polyethylene glycol (PEG) was used as stabilizer. PEG molecules wrap around the nanoparticles to impart stability and prevent agglomeration, yet leave enough surface area available on the nanoparticle for catalytic activity. Our method is superior to others in terms of rapid generation and stabilization of Pd nanoparticles in water with a cheap, readily available PEG stabilizer. The size of the nanoparticles generated can be controlled by the concentration of PEG in water medium. The size decreased with the increase in the PEG: Pd ratio. This aqueous nano-sized Pd is a highly efficient catalyst for Suzuki, Heck, Sonogashira, and Stille reaction. Water is used as the only solvent for the coupling reactions.

1. Introduction

Organic synthesis is routinely performed in non-aqueous solvents, be it in academic research laboratories or industrial production units. Lack of solubility of generally lipophilic organic or organometallic compounds in water compelled chemists to employ non-aqueous solvents. In contrast, nature, in its unique way, utilizes water for enzymatic transformations of all organic substrates. The use of water, the most abundant and non-toxic solvent for reactions is reclaiming its importance due to pressing environmental, economical, and safety concerns.[1] Current emphasis on green chemistry underscores the need for developing catalytic reactions, especially with involving precious metals as mediators, in aqueous medium.[2]

Palladium catalyzed carbon–carbon and carbon–heteroatom coupling reactions are extensively used in the synthesis of complex organic molecules.[3] In these reactions, either preformed Pd complexes like $(PPh_3)_4Pd$ are used where ligands are P and/or N donors or active Pd complexes are generated in situ.[4] Many of these ligands are expensive, toxic, and sensitive to air and a major challenge lies in the separation of product from expensive catalyst, much to the dismay of large-scale producers. As an alternative, solid supported Pd catalysts have been developed for several reactions.[5] Ionic liquids are said to provide a green alternative to conventional organic solvents,[6] but they are not devoid of toxicity. Efforts have been made, therefore, to develop a Pd catalytic system *free of organic solvent* for such reactions. Water-soluble, phosphine based ligands,[7] and phase-transfer catalysts[8] have been used in an aqueous–organic biphasic reaction, but they operate under rather harsh conditions.

Nanoparticle catalysis in *water* squarely addresses the issue of carrying out efficient reactions under environmentally benign conditions associated with *green chemistry* and also facilitates separation of products[9] from Pd colloids dispersed in water. Since catalysis takes place on metal surface, nanoparticles are much more reactive than the particulate metal counterpart due to their high surface to volume ratio.[10] In this paper, we report a combination of both these facets use of water as solvent and use of Pd nanoparticles, which are synthesized and stabilized in water[11] as catalyst for a variety of coupling reactions where predominantly lipophilic organic reactants provide high yield of products in water as the only solvent.

2. Experimental

2.1. General

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC). All ^1H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded on a Bruker-Avance DPX300 for a $CDCl_3$ solution and

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reported in parts per million (δ). UV–vis spectra were recorded on Evolution 300 (Thermo). TEM pictures were taken on a JEM-2011 (JEOL). Flash Column chromatography was performed with silica gel (230–400 mesh). All cross-coupling reactions were carried in water under air.

2.2. Preparation and characterization of Pd nanoparticles

The acyl metal salt[12] $(CO)_5W{=}C(Me)ONEt_4$ (0.002 g, 0.004 mmol) was dispersed into 4 mL of distilled water and added slowly in a drop wise manner into a well-stirred aqueous solution (6 mL) of K_2PdCl_4 (0.0032 g, 0.01 mmol) and polyethylene glycol (PEG 6000, 0.06 g, 0.01 mmol) (Scheme 1). This affords 1 mol % catalyst solution (Pd/PEG 6000 molar ratio=1:1) that has been used throughout the study.

The yellow color of the Pd(II) solution (λ_{max} 415 nm) immediately changed into dark brown indicating formation of Pd nanoparticles as characterized by UV–vis spectrum (Fig. 1).

The absorption peak (λ_{max} 415 nm) gradually flattened with incremental addition of Fischer carbene complex with concomitant increase in the intensity of absorption (Fig. 1, curve A to K). After complete addition of the Fischer carbene salt, a broad band developed without any peak, which is characteristic of colloidal palladium (Fig. 1). Transmission Electron Microscopy (TEM) pictures were taken with different concentration of PEG 6000, which confirmed the generation Pd nanoparticles with a spherical shape and an average diameter of 7–10 nm (Fig. 2).

The selected area electron diffraction (SAED) pattern (Fig. 3b), exhibited four diffused rings, which were assigned to the (111), (200), (220), and (311) reflections of *fcc* Pd and confirms the crystalline nature of nanoparticles. The lattice spacing value of 0.224 nm in the high-resolution transmission electron microscopy (HRTEM) image (Fig. 3a) matched very well with the (111) lattice plane of palladium metal. The colloidal Pd was stable in aqueous medium and no precipitate was observed for months.

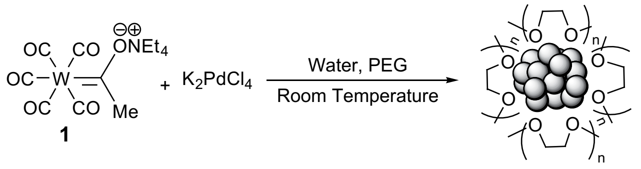
2.3. Size control of Pd nanoparticles by variation of amount of PEG

Earlier we have shown that the size of Au nanoparticles generated by this method can be controlled by varying the chain length of OEG or PEG.[13] In the case of palladium, we used PEG in different concentrations with respect to K_2PdCl_4 like 1:1, 1:2, 1:3, 1:4, and 1:5 to see if it affected the size of Pd nanoparticle. The gradual variation in size of nanoparticles with different PEG 6000 molar concentration is revealed clearly in the TEM pictures (Fig. 2A–E). The hyperbolic nature of the curve obtained from the plot of the size of Pd nanoparticle against PEG concentration (Fig. 4), implies that size of the nanoparticle decreased gradually with the increase in PEG concentration and a limiting value is reached as the surface of the particles get saturated with the capping agent.

2.4. Pd nanoparticle catalyzed reactions in water

2.4.1. *Suzuki reaction of aryl halides*

To a mixture of aryl halide (1 mmol), boronic acid (1.2 mmol), and K_2CO_3 (2 mmol), 10 mL of the catalyst solution (1 mol %) in water was added. The reaction mixture was then stirred at the specified temperatures for 10 min to 8 h (see Table 1). After cooling to room temperature, the reaction mixture was extracted thrice with diethyl ether (15 mL) and washed with water (10 mL). Then the organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum. The products were purified by flash column chromatography using either petroleum ether or ether (10–15%)/petroleum ether.



Scheme 1. Preparation of Pd nanoparticles in water with acyl metal carbene salt **1**, $(CO)_5W{=}C(CH_3)ONEt_4$ and K_2PdCl_4 using PEG 6000 as stabilizer.

2.4.2. *Heck reaction of aryl halides*

The catalyst solution (2 mol %) in water was added to an RB flask containing the aryl bromide (1 mmol), alkene (1.2 mmol), and K_2CO_3 (2 mmol). The reaction mixture was stirred at 100 °C for 12–14 h. After cooling to room temperature, the reaction mixture was extracted with ether (3×15 mL) and washed with water (10 mL), and then the organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum. The products were purified by flash column chromatography using either petroleum ether or acetone (2–4%)/petroleum ether.

2.4.3. *Sonogashira reaction of aryl halides*

The catalyst solution in water (1 mol %) was added to the aryl iodide (1 mmol), acetylene (1.2 mmol), and K_2CO_3 (2 mmol) in an RB flask. The reaction mixture was stirred at 55–65 °C for 2–3.5 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3×15 mL) and washed with water (10 mL), and then the organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum. The products were purified by flash column chromatography using either petroleum ether or ethyl acetate (5–15%)/petroleum ether.

2.4.4. *Stille reaction of aryl halides*

The catalyst solution (10 mL, 1 mol %) in water was added to a mixture of aryl bromide (1 mmol), phenyltributylstannane (1.2 mmol), and K_2CO_3 (2 mmol). The reaction mixture was stirred at 80 °C for 2–3 h. After cooling to room temperature, the reaction mixture was extracted thrice with diethyl ether (15 mL) and washed with water (10 mL). Then the organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum. The products were purified by flash column chromatography using either petroleum ether or ether (10–15%)/petroleum ether.

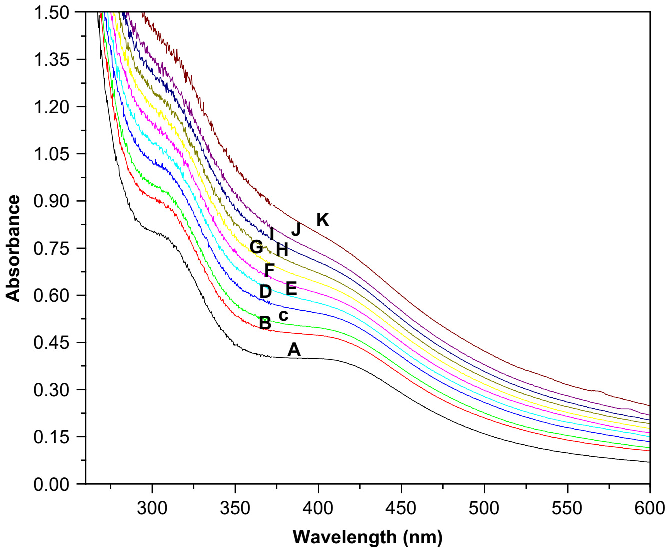


Figure 1. UV–vis spectrum taken after each addition of Fischer carbene salt suspension (0.1 mM) by 100 μL amount to K_2PdCl_4 solution (0.1 mM) (curve A) and gradual formation of Pd nanoparticles indicated from the curves B to K.

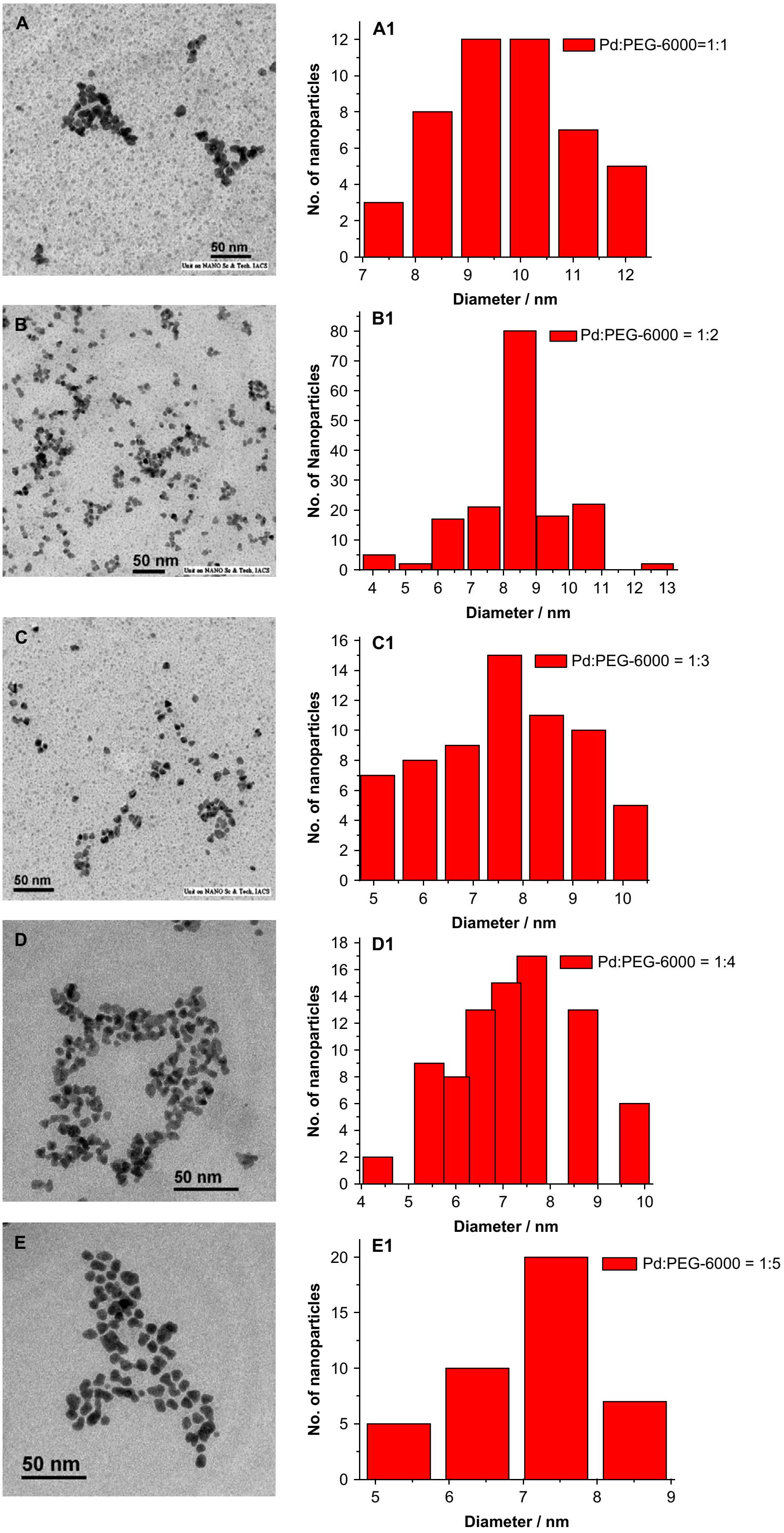


Figure 2. TEM pictures of Pd nanoparticles with varying Pd/PEG molar ratio (A) 1:1, (B) 1:2, (C) 1:3, (D) 1:4, (E) 1:5 and their corresponding size distribution graphs in A1, B1, C1, D1, E1.

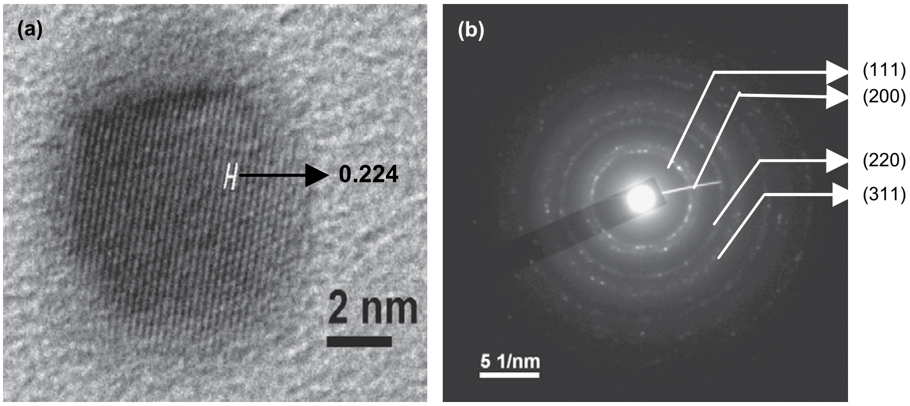


Figure 3. (a) High-resolution TEM of a single Pd nanoparticle and (b) SAED pattern of crystalline Pd nanoparticles.

3. Results and discussions

Palladium nanoparticle catalyzed coupling was pioneered by Reetz using surfactants as stabilizing agents.[14] Recently, EI-Sayed et al. reported the use of PVP stabilized Pd nanoparticles as efficient catalysts[15] for the Suzuki reaction in aqueous medium (40% EtOH or CH_3CN/H_2O), but this approach was to aryl iodides. Use of triblock copolymer in synthesis and stabilization of Pd nanoparticles recently reported by Hyeon and his group.[11b] Such polymer, dendrimer,[16] organic ligands,[17] and surfactant stabilized Pd nanoparticles[18] are being widely used for various coupling reactions but most of them use organic or ionic liquid as solvent, high temperature or microwave irradiation.[18,19] Recently it has been suspected in several 'ligand-modified' as well as 'ligandless' Pd systems,[20,21] the active catalytic species might be Pd nanoparticles formed in situ under the given reaction condition. Schmidt and Vries et al. have shown that $Pd(OAc)_2$ as catalyst precursor in very dilute solution gives good result at high temperature in Heck reaction with activated aryl halides.[22] But the scope of 'ligandless' catalyst recycle is limited by the fact that Pd nanoparticles eventually aggregate to form Pd black; hence it falls short of general implementation. Thus, it is still very challenging to develop a user-friendly process to synthesize metal nanoparticles that are stable in aqueous phase and use them for catalysis under mild conditions.

We established that the Fischer carbene complex is effective for generation of metal nanoparticles like Au and Pd in water in presence of an oligo or polyethylene glycol (OEG or PEG) additive, which serves as the stabilizing agent for the nanoparticles.[13] This protocol is extremely mild yet reliable for controlled generation of stable Pd nanoparticles in water at room temperature (Scheme 1). The Fischer carbene complex features tungsten metal in zero oxidation state and thus provides a source of soluble W(0) species. It transfers electrons to reduce other metals like Pd, Pt, Au or Ag and itself gets converted to W(III) state in this process.[†] PEG has shown its ability to stabilize due to its special molecular structure. Unlike in many reported instances of Pd nanoparticle catalysis where PEG has been used as a solvent[23] we limited the quantity of PEG to a few mol % and those Pd nanoparticles stabilized by PEG are highly effective as catalyst. Usually the dendritic polymer-bound Pd complexes execute low reactivity as catalyst because catalytic centers are rendered inaccessible by encapsulating polymer or surfactants[24] but, in our case PEG wrapping does not appear to adversely affect the reactivity of Pd nanoparticles.

We have already reported that such catalytic system is effective for Hiyama coupling reaction in water and that the rate of the reaction varies according to the size of the nanopartricles.[13] We have now extended this study to cover Suzuki, Heck, Stille, and Sonogashira couplings in order to extend their utility. We report herein the usefulness of Pd nanoparticles as catalyst for different cross-coupling reactions in water alone as solvent and without exclusion of air.

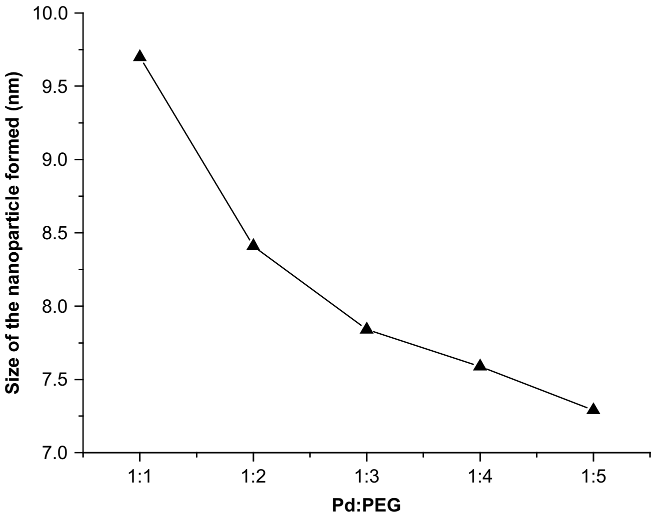


Figure 4. The graph obtained from average particle size with varying Pd/PEG ratio.

3.1. Suzuki reaction

The Suzuki reaction[25] in aqueous medium is known from a long time and it also has been used for sensitive substrates like unprotected halonucleosides.[26] Homogeneous Pd based catalysts were used in these instances. Use of Pd nanoparticle in Suzuki coupling in aqueous phase, on the other hand, has only a few precedents till date.[27] A nanoparticle suspension (0.01 mmol) prepared in 10 mL water was added drop wise to the reaction mixture by constant stirring using a magnetic stirrer at room temperature to check its catalytic activity for the reaction of phenylboronic acid with *p*-bromoacetophenone in DME/water (1:5 v/v). Gratifyingly, the reactants were fully converted into desired product (isolated yield 95% after purification) at room temperature within 3 h. In subsequent runs, use of DME as co-solvent was dispensed with and the reaction was performed in pure water with equally impressive yield and the reaction was complete within 2 h. A yield of 98% was obtained within 2 h when the reaction was

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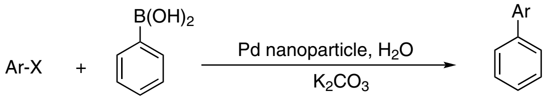
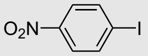
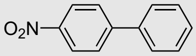
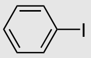
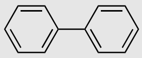
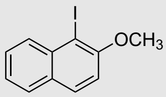
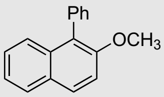
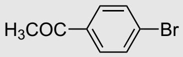
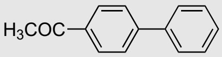
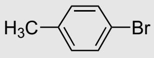
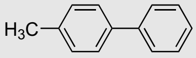
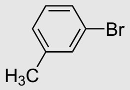
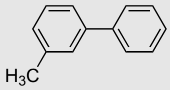
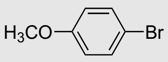
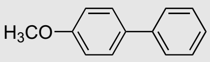
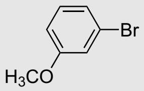
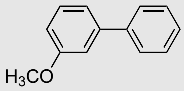
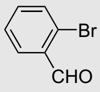
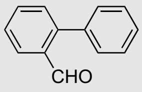
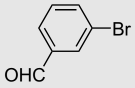
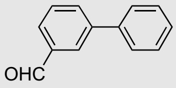
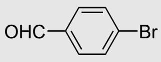
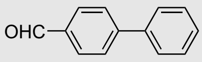
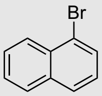
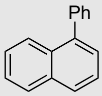
[†] The oxidation state of W(III) was not experimentally determined, but the stoichiometry of carbene complex and metal salt [for Pd(II), Pd/W 2:3, for Au(III), Au/W 1:1 etc.] suggests formation of W(III).

carried out at room temperature, establishing the superior catalytic efficiency of the nanoparticles in aqueous medium (Table 1).

A variety of substituted aryl bromides featuring either an electron-releasing or an electron-withdrawing group were then examined (Table 1). The electron-rich substrates like bromoanisole (entry 7) required 2 h for complete conversion at 25 °C. However, reaction of 1-chloro-4-nitrobenzene with phenylboronic acid did not afford any coupled product. An *ortho* substitution offers steric hindrance and requires elevated temperature for useful conversion (entries 3 and 9). For activated substrate like *p*-bromoacetophenone, the rapid reaction rate was insensitive to the base used. Less activated substrate like 4-bromoanisole was sensitive to the nature of base. Among the bases screened, K_2CO_3 was found to be more effective than triethylamine, NaOAc, $CsCO_3$, CsF, or CsOAc. After extraction of the product from *p*-bromoacetophenone and phenylboronic acid with ether (entry 4), the aqueous extract was recycled, albeit with gradual loss of catalytic efficiency (yield dropped from 90% to 40%).

Table 1
Pd nanoparticles catalyzed Suzuki coupling reaction with aryl halide and phenylboronic acid[a]



Entry	Substrate	Product	Temp (°C)	Time	% Yield[b]
1			25	10 min	98
2			25	30 min	98
3			60	3 h	91
4			25	2 h	98
5			25	2 h	90
6			25	3 h	92
7			25	2 h	98
8			40	4 h	90
9			60	8 h	85
10			60	4 h	95
11			60	8 h	87
12			60	4 h	92

[a] Reaction conditions: aryl halide (1.0 equiv), boronic acid (1.2 equiv), K_2CO_3 (2 equiv), water (4 mL), Pd nanoparticle in water (0.01 equiv, 6 mL) with PEG 6000 (1.0 equiv, 60 mg).

[b] Isolated yield after purification by flash column chromatography (eluent: petroleum ether or ether/petroleum ether).

3.2. Heck reaction

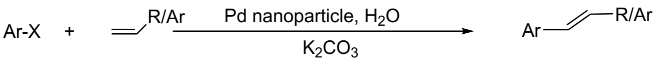
One of the most important Pd catalyzed coupling reaction is vinylation of aryl halides, known as the Heck reaction.[28]

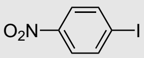
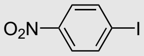
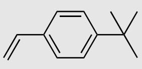
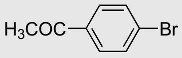
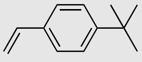
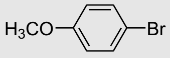
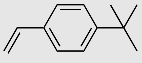
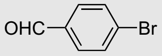
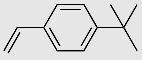
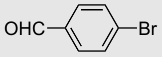
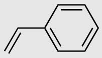
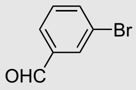
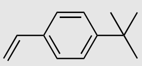
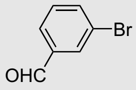
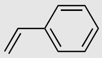
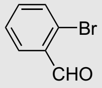
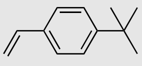
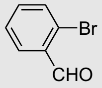
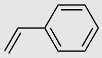
It has been demonstrated that Pd nanoparticles catalyze Heck reactions with activated esters and aryl iodides either at elevated temperatures under ligand free condition[14f] or in presence of tetraalkylammonium bromide as stabilizer.[29] In our experiments, palladium nanoparticles stabilized by PEG displayed high catalytic activity in Heck arylation. For iodo- and bromoarenes, 2 mol % of Pd nanoparticle was adequate for a relatively unactivated partner like *tert*-butylstyrene (Table 2) in water under reflux. The requirement of a higher catalyst loading is compensated by the efficiency of the reaction and avoidance of organic solvent for the reaction (Table 2).

3.3. Copper-free Sonogashira reaction

The alkynylation of aryl halides, frequently called Sonogashira–Hagihara reaction[30] is another synthetically useful coupling reaction catalyzed by palladium(0). Application of this reaction (between a terminal alkyne and aryl halide) is to be found in

Table 2
Pd nanoparticles catalyzed Heck coupling reaction with aryl halide and alkene[a]

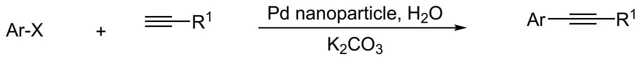


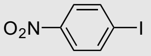
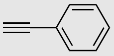
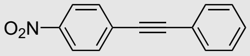
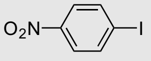
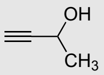
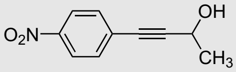
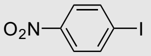
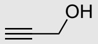
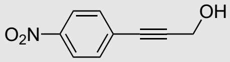
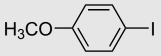
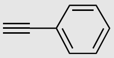
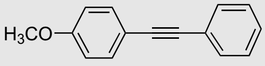
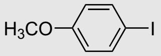
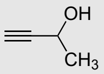
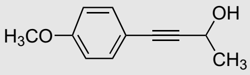
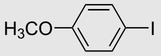
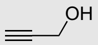
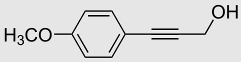
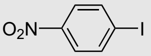
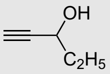
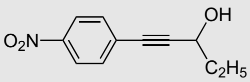
Entry	Aryl handle	Alkene	Temp (°C)	Time (h)	% Yield[b]
1			80	6	92
2			100	10	92
3			100	10	90
4			100	14	70
5			100	12	80
6			100	12	75
7			100	12	5
8			100	12	74
9			100	12	80
10			100	12	72

[a] Aryl bromide (1 mmol), alkene (1.2 mmol), K_2CO_3 (2 mmol), water (4 mL), Pd nanoparticle in water (0.02 equiv with PEG 6000 2.0 equiv 120 mg).

[b] Isolated yield after purification by flash column chromatography (eluent: petroleum ether or acetone/petroleum ether).

Table 3
Pd nanoparticles catalyzed Sonogashira coupling reaction with aryl halide and alkyne[a]



Entry	Aryl iodide	Alkyne	Product	Time (h)	% Yield[b]
1				2[c]	95
2				3.5[c]	95
3				2[c]	92
4				5[d]	94
5				5[d]	88
6				3.5[d]	90
7				3.5[d]	90

[a] Aryl bromide (1 mmol), alkyne (1.2 mmol), K_2CO_3 (2 mmol), water (4 mL), Pd nanoparticle in water (0.01 equiv with PEG 6000 1.0 equiv).
[b] Isolated yield after purification by flash column chromatography (eluent: petroleum ether or ethyl acetate/petroleum ether).
[c] Reaction temperature is 55 °C.
[d] Reaction temperature is 65 °C.

synthesis of numerous natural products including enediyne antibiotics.[31] Although copper(I) has been initially used as co-catalyst with an amine as solvent as well as base, a few copper-free procedures were subsequently developed[32] but they usually required ultrasound or microwave activation.

The only report for Sonogashira reaction carried out in water alone[33] prescribes phosphine ligands for palladium as catalyst and use of Cu(I).

Our catalytic system is a unique and operationally simple procedure that is conducted in pure water *without* Cu(I) salt, phosphine or amine ligand for palladium and any precaution to exclude air. No surfactant or organic co-solvent was required. High yields were obtained at 55–65 °C for iodoarenes (Table 3). Since no copper salt was used, the undesired formation of oxidative homocoupling product, a diyne, was also avoided. Although the reaction proceeded well with aryl iodides, it was a disappointment that no coupling product was formed with activated bromides like 4-bromoacetophenone even at elevated temperature under a wide range of conditions varying the solvent and the base (Table 3).

3.4. Stille reaction

In this coupling reaction the organometallic coupling partner is an organostannane that is air and moisture stable, which reacts with aryl halides.[34]

In majority of instances, Stille reaction with bromo or iodoarenes has been performed in aqueous solvent using $RSnCl_3$.[35] A few articles that report on Stille reactions catalyzed by Pd nanoparticles, describe the use of quaternary ammonium salts as stabilizer and solvent[36,16e] or ionic liquid as solvent for Pd nanoparticles generated in situ.[37] Crook et al. used dendrimer bound Pd nanoparticles in water as catalyst at room temperature for this reaction;[16e] the bromoarenes required about 10-fold increase in the quantity of catalyst to match the efficiency achieved with iodoarenes. With our catalytic system, we were able to obtain biaryls even from moderately activated bromo substrates and phenyltributylstannane in aqueous medium at 80 °C with K_2CO_3 as base. There was no need for careful exclusion of air (Table 4).

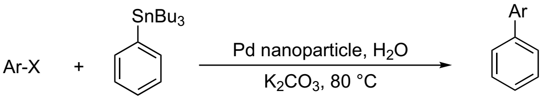
4. Conclusion

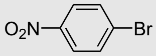
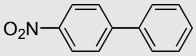
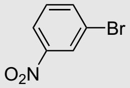
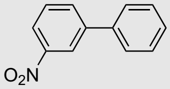
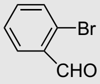
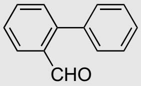
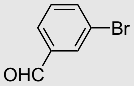
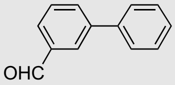
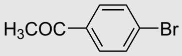
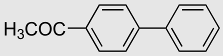
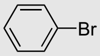
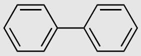
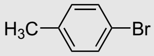
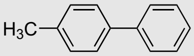
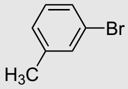
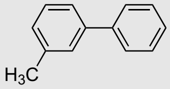
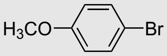
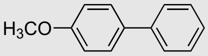
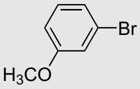
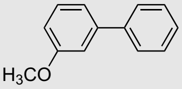
The generation and stabilization of catalytically active nanoparticles in water have several important advantages over both traditional homogeneous and supported transition-metal catalysts in terms of lower cost, absence of expensive ligands and organic solvents. It combines high activity of the homogeneous system with potential of recovery and recycling as practiced with heterogeneous catalysts. Here, PEG act as stabilizer, which absorb to the particle surface, control particle size, and prevent agglomeration. Water is an excellent solvent for this PEG capped nanoparticles in catalytic system. Possibly the polar capping agent forms a more open structure in water, so that reactants could easily get into contact with the metal surface. This is a favorable situation for catalysis since strong encapsulation could lead to loss of catalytic activity.

In conclusion, we have successfully illustrated that PEG stabilized Pd nanoparticles (obtained from reaction of a Fischer carbene complex of tungsten with K_2PdCl_4 at room temperature) have a narrow size distribution and the size can be controlled varying the PEG concentration in water. Those nanoparticles displayed high catalytic activities toward Suzuki, Heck, Sonogashira, and Stille reactions in water alone as solvent under mild condition. No care to exclude air was necessary. We are currently looking forward to utilize this catalytic system for biological applications in water. We also plan to investigate synthesis and utility of chiral PEG scaffold in

Table 4

Pd nanoparticles catalyzed Stille coupling reaction with aryl halide and phenyltributylstannane[a]



Entry	Substrate	Product	Time (h)	% Yield[b]
1			2	95
2			2	98
3			2	95
4			2	95
5			2	95
6			2	90
7			3	88
8			3	95
9			3	92
10			3	98

[a] Aryl bromide (1 mmol), phenyltributylstannane (1.2 mmol), K_2CO_3 (2 mmol), water (4 mL), Pd nanoparticle in water (0.02 equiv with PEG 6000 1.0 equiv). All reactions are performed at 80 °C.

[b] Isolated yield after purification by flash column chromatography (eluent: petroleum ether or ether/petroleum ether).

asymmetric synthesis involving Pd nanoparticle-mediated coupling reactions.

Acknowledgements

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Supplementary data

Supplementary data (contains copies of ^{1}H and ^{13}C NMR spectra of all products listed in the tables) associated with this article provided as a separate file. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.03.062.

References and notes

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