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Sonogashira reactions catalyzed by water-soluble, β-cyclodextrin-capped palladium nanoparticles

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The Sonogashira reaction was efficiently catalyzed by β-cyclodextrin-capped Pd nanoparticles (β-CD/Pd) in aqueous solution at room temperature. In addition, PPh_3 was not necessary to be present in the reaction media, and CuI, one major requirement for the typical homogeneous Sonogashira reaction, could be completely omitted without affecting the catalytic activity of β-CD/Pd nanoparticles. This study offers a new example of using β-CD-capped metal nanoparticles as a novel nanocatalyst for catalytic organic reaction in aqueous solution.

KEY WORDS: Sonogashira reaction; β-CD-capped Pd nanoparticles; aqueous media; nanocatalyst.

1. Introduction

The Sonogashira coupling, a palladium–copper–catalyzed reaction of aryl halides and terminal acetylenes, is one of the important and widely used sp^2–sp carbon–carbon bond formation reactions in organic synthesis, which gives an efficient route to alkyl–aryl and diaryl-substituted acetylenes [1]. It has been widely used for the synthesis of natural products [2], biologically active molecules [3], molecular electronics [4], dendrimers and conjugated polymers [5–10] because of its wide tolerance to functional groups and the availability of common aryl halides. The reaction is generally conducted in organic solutions in the presence of an amine base, copper(I) iodide as a co-catalyst and a homogeneous palladium catalyst such as $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$, which makes the separation and the recovery of the catalysts tedious and might result in high palladium contamination of the products. Heterogeneous solid-supported palladium catalysts have been used to overcome these difficulties [1]. They include palladium on charcoal, zeolites and magnesium oxide [11–14], Pd-modified mesoporous catalyst [15], and $[Pd(NH_3)_4]$–NaY [16]. The potential advantages of the systems include the ease of separation, facile recycling of the metal and the low level of metal contamination in the product. Copper-free Sonogashira reactions have been developed to overcome an important side reaction in the presence of a Cu(I) co-catalyst [12,14–22], which reduces Glaser-type homocoupling reactions of terminal alkynes to diynes in the presence of oxygen. However, the development of simpler, more economic and efficient catalysts is still an important topic in this area.

Nanoparticle-based materials are increasingly investigated as new types of homogeneous or heterogeneous catalysts (also called nanocatalysts) for various reactions in different media [23–28]. Advantages of metal nanoparticles as homogeneous nanocatalysts (HomoNC) include the highly economic efficiency due to their large surface-to-volume ratio, and enhancement of the reaction rate through elimination of the diffusion barrier existing in typical heterogeneous catalytic systems [26]. Copper- and ligand-free Sonogashira reaction catalyzed by Pd nanoparticles were reported in acetone and ethanol solutions [29,30]. Thathagar *et al.* reported ligand-free Sonogashira Cross-Coupling catalyzed by metal clusters (Cu, and Pd) in DMF solution at elevated temperature [31,32]. Gao, *et al.* used palladium nanowires for efficient Sonogashira coupling reaction in isopropanol at 75 °C. In this work, we report that water-soluble β-cyclodextrin-capped Pd (β-CD/Pd) nanoparticles work as an active HomoNC for copper-free and phosphine-free Sonogashira coupling reactions for non-polar substrates at room temperature. The presence of β-cyclodextrin on Pd nanoparticles might enhance the overall reaction efficiency. This work presents a new example of using β-cyclodextrin-capped metal nanoparticles for catalytic organic reaction in aqueous solution.

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2. Experimental

2.1. Materials

All compounds and solvents used in the work are commercial products (from Aldrich or Acros) with the highest quality available unless notified in the following context. Deionized and doubly distilled water was used throughout all the experiments. Silica gel (400 mesh) for the column chromatography was purchased from Matland International Corporation. The deuterated solvents for NMR study were obtained from Cambridge Isotope. Carbon-coated copper grids (400 mesh) for TEM measurement were from Ted Pella.

2.2. Preparation of β-cyclodextrin-capped palladium nanoparticles (β-CD/Pd nanoparticles)

The procedure used in this work to prepare β-CD/Pd nanoparticles was slightly modified from the one reported before [33]. In a typical preparation, 146.8 mg of Na_2Cl_4Pd and 91.2 mg of perthiolated β-cyclodextrin were dissolved in 80 mL of dimethylformamide (DMF) [34]. This solution was then divided into 4 parts. 302 mg of $NaBH_4$was dissolved in 80 mL of DMF. An aliquot of 20 mL from this $NaBH_4$ solution was added quickly to the each of the Pd solution under N_2 atmosphere with fast stirring. The reaction was kept overnight. DMF was then removed by centrifugation. The residue was washed with 100 mL of DMF for 4 times and subsequently with 100 mL of ethanol/water (90/10) mixed solvent. The final product was re-dissolved in 5 mL of pure water in a 100 mL round bottom flask and freeze-dried to yield deep brown powder.

2.3. Aqueous Sonogashira reactions catalyzed by β-CD/Pd nanoparticles

In a typical reaction, an aryl halide (2.0 mmol) and a terminal alkyne (2.5 mmol) were reacted in 10 mL of H_2O in the presence of 10% (mole) of β-CD/Pd and 5 mL of diisopropylamine under a nitrogen atmosphere at room temperature for 20 h. The reaction mixture was then diluted with water and extracted with EtOAc three times. The combined organic phase was washed with saturated NaCl aqueous solution two times and dried over anhydrous $MgSO_4$. The solvent was removed and crude product was purified by chromatography (Silica gel) to give pure target compound. The final product was identified by ^1H and ^{13}C NMR.

2.4. Surface coverage measurement

The surface coverage of β-CD on each nanoparticle was 50%. The calculation was based on the following information, (1) the weight and the surface area of each nanoparticle by using the average particle size obtained from TEM measurement, (2) the MW of perthiolated β-CD, (3) projected surface area (~ 180 $Å^2$) of each β-CD molecule [34], (4) the weight percentage of Pd and C from the elemental analysis.

2.5. Determination of turn over frequency (TOF)

The turn over frequency (TOF) of a typical Sonogashira reaction was calculated by obtaining the yield of the reaction each hour in first five hours from the GC-MS measurement.

2.6. TEM measurements

The TEM measurements were carried out on a JEOL4000FX instrument. A few drops of β-CD/Pd nanoparticle aqueous solution were transferred onto a carbon coated copper grid. The water was naturally evaporated at room temperature. The TEM images were obtained at 200 KeV acceleration voltages respectively. The average particle size was estimated by counting over 100 individual particles from a typical TEM image.

2.7. NMR

NMR spectra (400 MHz) were recorded with a Varian UI400 NMR spectrometer. ^1H NMR spectra of free β-CD and surface-anchored β-cyclodextrin on Pd nanoparticles were obtained in D_2O. ^1H and ^{13}C spectra of the final product from the Sonogashira reaction were obtained by using $CDCl_3$ as the solvent.

2.8. GC-MS

GC/MS experiments were carried out on a Shimadzu QP 5050A Gas Chromatograph/Mass Spectrometer with CI-50 chemical ionization controller. Ethylacetate was used as the solvent. Each experiment was carried out for 20 min and data was recorded from 3 min to 20 min.

3. Results and discussion

3.1. Preparation and characterization of water-soluble, β-cyclodextrin-capped palladium nanoparticles (β-CD/Pd nanoparticles)

A single-step and one-pot approach was used to prepare β-CD/Pd nanoparticles. The nanoparticles were prepared by the reduction of Pd salt by $NaBH_4$ in the presence of perthiolated cyclodextrin in DMF solution. Figure 1 shows a typical TEM image and the size distribution of β-CD/Pd nanoparticles. The average particle size was estimated as 3.2 ± 0.8nm in diameter. These surface-modified nanoparticles are highly soluble in water. Surface modification of Pd nanoparticles with β-CD was further verified by ^1H NMR spectra of the nanoparticles in D_2O solution. Figure 2 displays the ^1H NMR spectra of free β-CD and β-CD/Pd nanoparticles. The broadening of proton signals from surface-anchored β-CD was believed to the results of fast

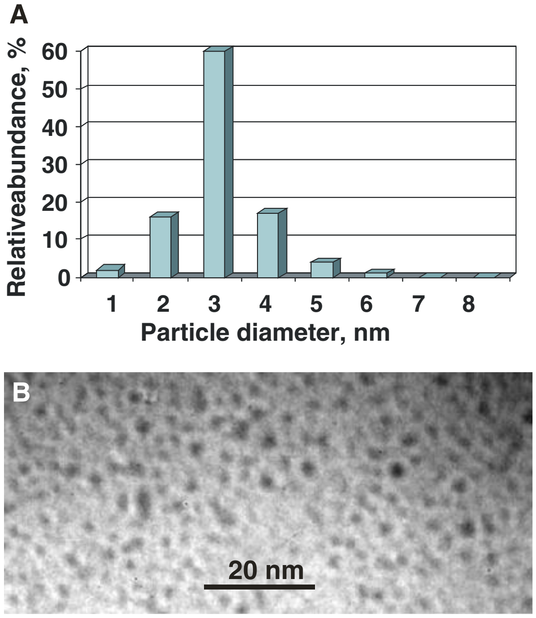


Figure 1. The size distribution (A) and a typical TEM image (B) of β-CD/Pd nanoparticles.

relaxation and heterogeneous environment of these molecules. Similar phenomena were also observed in other organic molecule-protected nanoparticles [35].

The high solubility of the nanoparticles in the water is attributed to the existence of many hydroxyl groups of surface-attached β-CDs on the nanoparticles. According to the elemental analysis and TEM measurement, β-CD molecules cover ~50% of the total surface of each nanoparticle. Thus, the covalent attachment of β-CD to Pd nanoparticles produces a robust and isolable nanomaterial which can be dissolved and then re-collected from water without losing its stability since up to seven thiol groups of each β-CD derivative are attached to Pd nanoparticles [39]. Compared with other organic protectors, the bulky β-CD molecules on nanoparticle surface not only protect the nanoparticles from the agglomeration, but also keep some fraction of nanoparticle surface unpassivated and available to participate in the catalytic reactions. Considering that β-CD is a well-known host for small non-polar organic species [36], the modification of Pd nanoparticles with β-CDs can incorporate two functions of catalyst and molecular recognition into one package [33,37–40]. Inclusion of hydrophobic organic substrate inside the surface-anchored β-CD leads to the placement of these molecules on the vicinity of particle surfaces [33,37–40]. Thus, the catalytic process is expected to be facilitated on Pd particle surfaces. In the consideration of the unique features of β-CD/Pd nanoparticles with the current interest in the application of metal nanoparticles as catalysts, the Sonogashira reaction catalyzed by these water-soluble β-cyclodextrin-capped palladium nanoparticles as ‘‘soluble’’ analogues of heterogeneous catalysts in aqueous media was explored in this work.

3.2. Investigation of reaction conditions for the Sonogashira couplings catalyzed by β-CD/Pd nanoparticles in aqueous media

The Sonogashira reaction is one of the most important carbon-carbon coupling reactions [1,41] and has a variety of applications in many fields, from the preparation of molecular wires [4] to natural product synthesis [2]. In this type of reaction, coupling of terminal alkynes with aryl or alkenyl iodides produces arylalkynes and conjugated enynes [1]. The Sonogashira reaction is typically carried out in the presence of a palladium complex and copper iodide as catalyst and co-catalyst respectively [1]. Amine and phenylphosphine are typically used as the base and stabilizing agent for palladium complex [1]. Thus, our initial test on the Sonogashira reaction by using β-CD/Pd nanoparticles as the HomoNC in aqueous media consisted of all typical components, *e.g.*, PPh_3 as stabilizing agent, CuI as

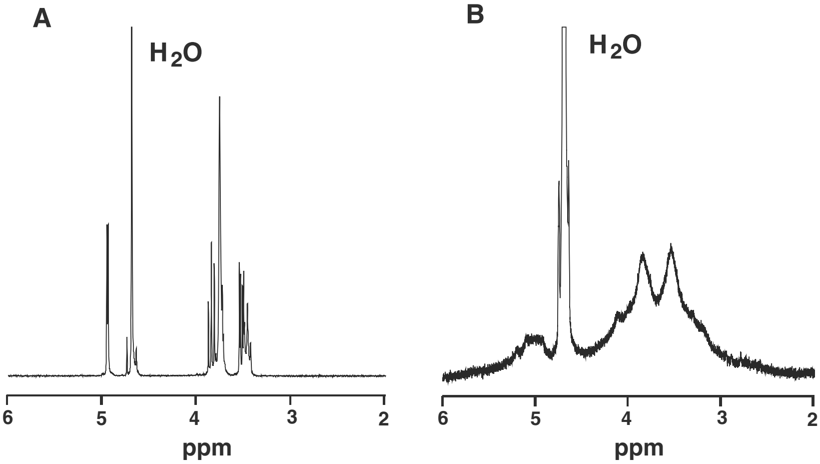


Figure 2. ^1H NMR of (A) free β-CD and (B) β-CD on Pd nanoparticles in D_2O.

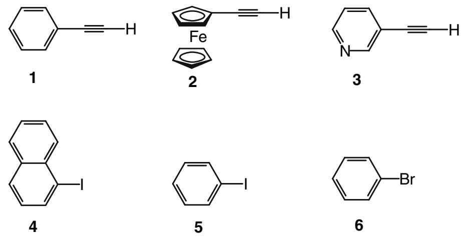


Chart 1. Substrates for aqueous Sonogashira reactions.

co-catalyst and diisopropylamine as the base. No organic solvent was used in the reaction mixture. Phenylacetylene (**1**) and iodobenzene (**5**) were used as the representatives for terminal alkyne and aryl iodide (chart 1) in the initial test.

The reaction was performed under a N_2 atmosphere at 45 °C for 20 h. We soon found out that PPh_3 was not necessary to be present in the reaction by running a control experiment in the absence of PPh_3 under the identical conditions. In both cases, the final yield of the product was the same (~90%) within the experimental error. In addition, the reaction still offered a satisfactory yield (~90%) when it was carried out at room temperature (25 °C) for 20 h (table 1). It should be noted that the Sonogashira reaction catalyzed by supported Pd nanoparticles under the ligand free condition was also found by other researchers [12,17,22,29,30,42,43]. In addition, several groups reported that some Sonogashira reactions could be successfully carried out under the copper free condition [12,16–19,21,22,30,43,44]. Stimulated by these results and the attempt to further simplify the reaction condition, we took one more step. CuI was also removed from the reaction mixture. But the same reaction still reached a satisfactory yield (89%) after 20 h at room temperature (table 1). Thus, we concluded that *β*-CD/Pd nanoparticles could be used as an efficient catalyst for the Sonogashira reaction in aqueous media without stabilizer and co-catalyst (scheme 1). In order to assess the catalytic activity of the *β*-cyclodextrin-capped palladium nanoparticles [33], the turn over frequency (TOF) of the Sonogashira reaction between **1** and **5** was estimated by GC-MS analysis. A linear relationship between the amount of product and reaction time was found in the first five hours (figure 3).

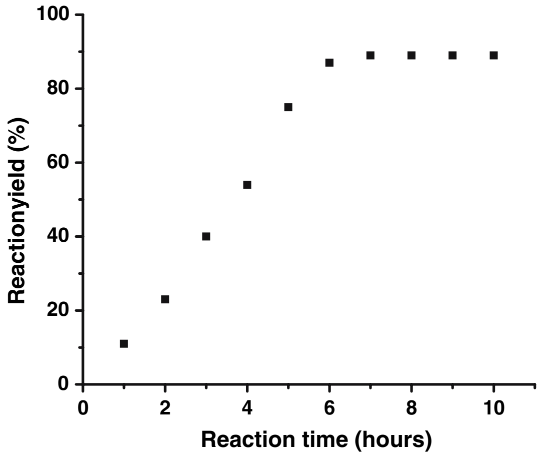
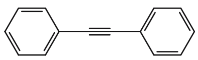
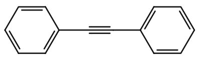
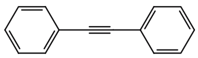
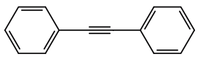
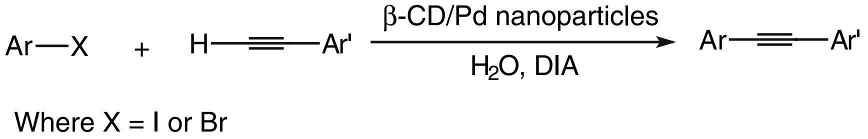


Figure 3. Relationship between the amount of product and reaction time.

Table 1
Catalytic activity of *β*-CD/Pd nanoparticles for aqueous Sonogashira reactions in the absence and presence of CuI and PPh_3[a]

Entry	Terminal alkyne	Aryl iodide	PPh_3	CuI	Product	Isolated yield (%)
1	**1**	**5**	Presence	Presence		90
2	**1**	**5**	Presence	Absence		90
3	**1**	**5**	Absence	Presence		90
4	**1**	**5**	Absence	Absence		89

[a] 10% (mole) *β*-CD/Pd for 20 h at room temperature.



Scheme 1. The aqueous Sonogashira reactions catalyzed by *β*-CD/Pd nanparticles.

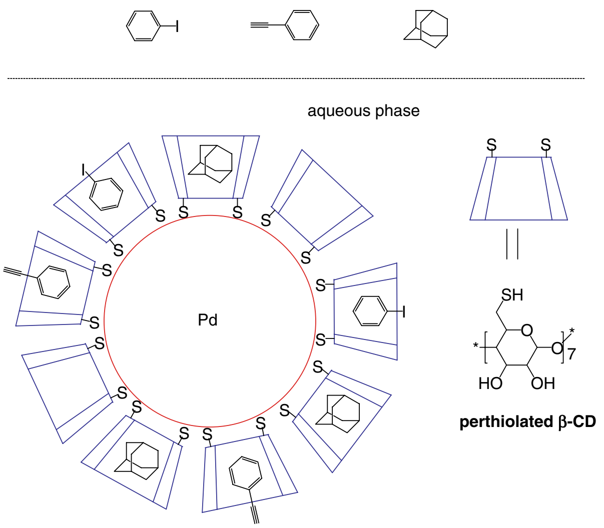
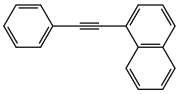
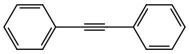
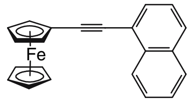
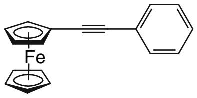
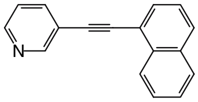
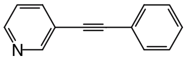
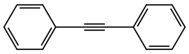
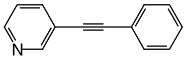
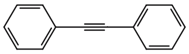


Figure 4. Inclusion of hydrophobic substrates inside β-CD molecules on the surface of Pd nanoparticles in the aqueous solution.

3.3. Potential Role of β-CD on Pd nanoparticles in the aqueous Sonogashira reaction

It is noted that all the reacting substrates are hydrophobic, which have very little solubility in water. Meanwhile, β-CD/Pd nanoparticles are highly soluble in aqueous solutions. In addition, the amine presenting in the reaction serves as another phase. Theoretically, there is a big kinetic barrier for this catalytic reaction. The substrates need to access the surface of Pd nanoparticles before having the catalytic process. The excellent yield of β-CD/Pd nanoparticles catalyzed Sonogashira reactions in aqueous media with these hydrophobic substrates might be related to the presence of β-CD on Pd nanoparticles. As demonstrated before [33,39,45], β-CD on nanoparticle surfaces acts not only as the protection ligands to prevent particle agglomeration, but also the artificial host for organic substrates in aqueous media. Thus, a possible mechanism to explain the efficiency of the catalytic process is proposed.

Table 2
Catalytic activity of β-CD/Pd nanoparticles for aqueous Sonogashira reactions[a]

Entry	Terminal alkyne	Aryl halide	Product	Isolated yield (%)
1	**1**	**4**		92
2	**1**	**5**		89
3	**2**	**4**		87
4	**2**	**5**		84
5	**3**	**4**		93
6	**3**	**5**		88
7	**1**	**6**		58
8	**3**	**6**		52
9	**1**in the presence of adamantine	**5**		18

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[a] 10% (mole) β-CD/Pd for 20 h at room temperature.

Inclusion of hydrophobic substrates inside the cavities of β-CD molecules on Pd nanoparticles brings these guest molecules to the vicinity of reacting sites on Pd surfaces, which might facilitate the overall catalytic process (figure 4). To test this possibility, adamantane was introduced as an inert competing substrate in the Sonogashira reaction since it is an excellent guest molecule for β-CD in aqueous solutions and has a high binding constant with β-CD [33,46–48]. Under the identical reaction conditions, the yield of the Sonogashira reaction with the substrates **1** and **5** in the presence of the same mole of adamantane was dramatically decreased to the one-fifth of the original value (table 2, entries 2 and 9). Inclusion of adamantane inside the β-CD on Pd nanoparticles could reduce the accessibility of this host to the hydrophobic substrate. Consequently, the overall concentration of active species for the Sonogashira reaction on Pd nanoparticle surfaces might decrease, which led to the low efficiency of the catalytic process. β-CD on Pd nanoparticle surfaces might act as a phase transfer catalyst, shuttling the hydrophobic substrates for the Sonogashira reactions in the aqueous media. The presence of adamantane would not have significantly affected the reaction yields if the Sonogashira reaction were catalyzed by leaching Pd atoms from β-CD/Pd nanoparticles [32,49].

3.4. *β-CD/Pd nanoparticles catalyzed Sonogashira couplings of terminal acetylenes with aryl halides in aqueous media*

By using the above established reaction conditions, the investigation of the Sonogashira coupling catalyzed by β-CD/Pd was extended to other aryl iodides and terminal acetylenes in water (chart 1). Sonogashira reaction proceeded smoothly at room temperature even in the absence of copper cocatalyst and phosphine ligands to afford the products with excellent isolated yields (table 2), which display similar yields obtained by the regular catalytic Sonogashira reactions in organic solvents carried out at room temperature. It is noted that catalyst loading in each reaction was not optimized since the goal of this study was to establish a general protocol for room-temperature Sonogashira coupling reaction in aqueous media. The efficiency of aryl bromides as a coupling partner under ligandless and copper-free conditions was also investigated (table 2, entries 7 and 8). The Sonogashira couplings of aryl bromides were a relatively slower with lower yields under the same conditions.

Pd nanoparticles supported on layered double hydroxide and Merrified resin, were reported to offer a good catalytic yield for Sonogashira reaction at an elevated temperature in a THF/H_2O mixed solvent [50]. It should be noted that other than water, ionic liquid is also a good choice of reaction media in term of catalyst recycling for the Sonogashira reactions [20,22,29].

4. Conclusion

The Sonogashira reaction was efficiently catalyzed, for the first time, with receptor-modified metal nanoparticles in aqueous media under a mild condition. The elimination of catalyst stabilizer and co-catalyst rendered a reaction condition in current study much simpler than most regular Sonogashira reactions carried out in organic solvent. In addition, eliminating organic solvent in the Sonogashira reaction represents a successful effort to perform organic reactions with a cleaner manner. The host-guest recognition might facilitate the overall catalytic process on β-CD/Pd nanoparticle surfaces in aqueous solution.

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