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Article

Simple synthesis of sub-nanometer Pd clusters: High catalytic activity of Pd/PEG-PNIPAM in Suzuki reaction

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ABSTRACT

Ultra-small metal nanoclusters have high surface energy and abundant active sites, and therefore their catalytic activities are usually significantly higher than those of larger nanoparticles. A temperature-responsive copolymer, namely poly(ethylene glycol)-*co*-poly(*N*-isopropylacrylamide) (PEG-PNIPAM) was synthesized as the first step, and then ultra-small Pd clusters stabilized within PEG-PNIPAM copolymer micelles were formed by direct reduction. Pd nanoclusters of size less than 2 nm showed outstanding catalytic activity in the Suzuki coupling reaction. The reaction between iodobenzene and phenylboronic acid was completed in as little as 10 s (turnover frequency = 4.3 × 10^4 h^{-1}). A yield of 64% was achieved in 5 min in the reaction between chlorobenzene and phenylboronic acid. The catalyst showed significant deactivation during three consecutive runs. However, this composite catalyst consisting of Pd/PEG-PNIPAM can be easily recycled based on the reversible phase transition of temperature-responsive PEG-PNIPAM. This catalyst therefore has good potential for practical applications.

1. Introduction

Ultra-small metal clusters are among the best heterogeneous catalysts. Their high surface energies and surface-to-volume ratios give them high atom efficiencies [1–4]. In some cases, the catalytic activities of small nanoclusters of certain critical sizes are significantly higher than those of larger nanoparticles. For noble-metal clusters, the critical diameter is around 2 nm [5–8]. These sub-2-nm nanoparticles have outstanding catalytic activities in many organic reactions such as the Suzuki reaction [8,9] and propene epoxidation [10]. However, these small metal clusters are more difficult to synthesize and use in practical applications than are larger nanoparticles. These clusters often suffer from significant corrosion and have poor stabilities [11]. Several synthetic methods such as impregnation, hydrothermal reduction, and radiolysis have been used to produce sub-nanometer Pd clusters [12–15]. In these methods, stabilizers such as functionalized polymers [16–18], dendrimers [19], and metal–organic frameworks [20] are generally used to stabilize the catalyst because their functional groups have high affinities with $PdCl_4^{2-}$, and this prevents agglomeration of the newly formed Pd clusters [21].

The Suzuki cross-coupling reaction between an aryl halide and an arylboronic acid is an important process in modern organic synthesis and offers a reliable pathway for the construction of aryl–aryl bonds. Suzuki reactions involving inactive

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but inexpensive aryl halides such as aryl chlorides are an attractive goal for the chemical industry. Generally, it is difficult to catalyze the reactions of aryl chlorides using heterogeneous Pd catalysts. The development of efficient heterogeneous catalysts for the reactions of aryl chlorides will be an important breakthrough [22–23].

Smart materials that respond to changes in their environment (e.g., pH and temperature) play important roles in catalysis [24–27]. Poly(*N*-isopropylacrylamide) (PNIPAM) is a temperature-responsive smart material; it shows a sharp phase transition in water at the lower critical solution temperature (LCST) [28–29]. Such smart polymers are excellent supports for noble metals, e.g., in Pd@PNIPAM [18], Pd-doped C/Co@PNIPAM-PPh_2 [27], hollow PNIPAM/Ag spheres [30–31], and Au@poly(glycidylmethacrylate-*co*-NIPAM) [32]. Noble-metal nanoparticles of size around 5 nm in such composites have shown good temperature-responsive catalytic behaviors, but their high catalytic activities have not been investigated.

In this study, we used single-electron-transfer living-radical polymerization (SET-LRP) [33] to synthesize a hydrophilic twin-tail polymer containing a poly(ethylene glycol) (PEG) ring and two linear PNIPAM chains. The PEG-PNIPAM chains can act both as reducing agents and catalyst supports in grafting ultra-small Pd nanoclusters to form a Pd/PEG-PNIPAM composite. The Pd/PEG-PNIPAM environment can be enriched with both hydrophilic and hydrophobic reactants, and therefore it shows extremely high catalytic activity in Suzuki cross-coupling reactions. The reaction between iodobenzene and phenylboronic acid in a mixture of ethanol and water (volume ratio of 1:1) was completed in 10 s (turnover frequency (TOF) = 4.3×10^4 h^{-1}) at 80 °C. The reaction with chlorobenzene gave 65% conversion in 5 min. The Pd/PEG-PNIPAM catalyst can be easily recycled because of the reversible phase transition of PNIPAM.

2. Experimental

2.1. Materials

PEG with two hydroxyl end groups (number-average molecular mass (M_n) = 1900 g/mol, Acros) was dried over anhydrous toluene by azeotropic distillation. *N*-Isopropylacrylamide (NIPAM, 97%, Kohjin Co., Japan) was recrystallized from a benzene/*n*-hexane mixture (65/35 *v*/*v*). Tris[2-(dimethylamino) ethyl]amine (Me_6TREN) was synthesized using a previously reported method [34]. 2-Chloropropionyl chloride and CuCl (99.99%) (Aldrich) were used as received, without further purification. Triethylamine was stirred for 12 h with KOH and then refluxed with toluene-4-sulfonyl chloride before use. Iodobenzene, phenylboronic acid, pentamethylbenzene (Alfa Aesar), and K_2CO_3 (Beijing Chemicals Co.) were analytical grade and used as received.

2.2. Reaction of PEG with 2-chloropropionyl chloride

In a typical synthesis, PEG (6.30 g, 1.58 mmol) was mixed with triethylamine (1.59 g, 15.80 mmol) and the mixture was cooled to 0 °C in an ice-water bath. A solution of 2-chloropropionyl chloride (1.98 g, 15.80 mmol) in benzene (10 mL) was added dropwise under stirring. The mixture was stirred at room temperature for 24 h. The sediment was removed by suction filtration and most of the benzene was volatilized by rotary evaporation. The solid was recrystallized from diethyl ether, and PEG with 2-chloropropionyl groups at both chain ends (PEG-2) was obtained by vacuum drying.

2.3. Preparation of PEG-PNIPAM by SET-LRP

A mixture of PEG-2 (1.00 g, 0.25 mmol), NIPAM (1.29 g, 11.50 mmol), and dimethylformamide (10.5 mL) was deoxygenated for 60 min by bubbling with nitrogen. After all the ingredients had dissolved, the tube containing the solution was immersed in liquid nitrogen. CuCl (45.50 mg, 0.46 mmol) and Me_6TREN (132 mg, 0.46 mmol) in water (7 mL) were added. The mixture was degassed by performing three freeze–pump–thaw cycles, and the tube was sealed under vacuum. The sealed tube was kept at 25 °C for 24 h; polymerization was achieved under stirring with a magnetic stirrer at 800 rpm. The mixture was purified by dialysis against distilled water to give a molecular-weight cut-off of 3500. Lyophilization gave PEG-PNIPAM as a white powder.

2.4. Pd nanoparticle loading on PEG-PNIPAM

PEG-PNIPAM (50 mg) was dispersed in distilled water (30 mL) and the dispersion was stirred for 10 min. $PdCl_2$ (0.0564 mol/L, 368 μL) was added and the mixture was stirred for 5 h. The mixture was purified by dialysis against distilled water to remove H^+, Cl^-, and Pd^{2+} ions. Lyophilization gave the Pd/PEG-PNIPAM composite as a light-brown powder.

2.5. Suzuki cross-coupling reaction

The Pd/PEG-PNIPAM catalyst (3 mg) was dissolved in water (3 mL). Iodobenzene (0.15 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (0.3 mmol), and pentamethylbenzene (0.15 mmol) were added to ethanol (3 mL) under stirring. The two solutions were mixed under magnetic stirring at a speed of 800 rpm and the reaction was performed at 80 °C in air. A sample of the reaction mixture was collected and analyzed using high-performance liquid chromatography (HPLC) and gas chromatography (GC).

2.6. Characterization

Gel-permeation chromatography (GPC; Waters 515 HPLC pump, Waters) was used to determine the molecular mass and polydispersity index of Pd/PEG-PNIPAM. The eluent was tetrahydrofuran (THF) at a flow rate of 1.0 mL/min at 40 °C. Polystyrene samples with narrow molecular mass distributions were used as calibration standards. Transmission electron microscopy (TEM; JEOL 1011F) was performed at 100 kV. Fourier-transform infrared (FTIR) spectroscopy (Thermo NICOLET iZ1) was performed using the KBr pellet method in the range

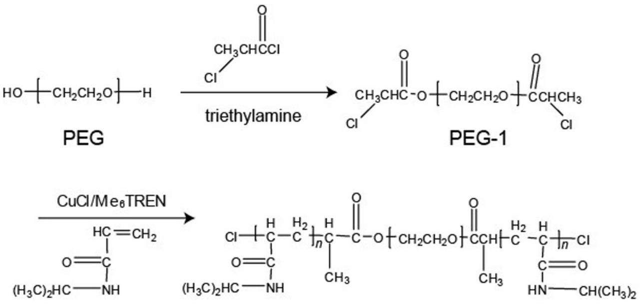
400–4000 cm^{-1}. The spectra were recorded in single-beam mode at a resolution of 4 cm^{-1}. Proton nuclear magnetic resonance (^{1}H NMR, 300 MHz) spectroscopy was performed using a Varian 400 MHz spectrometer at room temperature with $CDCl_3$ as the solvent. The Pd content of the catalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Shimadzu ICPE-9000). Elemental analysis was performed using X-ray photoelectron spectroscopy (XPS; ESCALab220i-XL electron spectrometer, VG Scientific) with 300 W Al K_α radiation. The temperature dependence of the optical transmittance of Pd/PEG-PNIPAM was investigated using ultraviolet-visible (UV-vis) spectroscopy (Shimadzu UV1601).

3. Results and discussion

3.1. Identification of PEG-PNIPAM structure

Linear PEG-PNIPAM played a key role in formation of the Pd/PEG-PNIPAM composite. It was synthesized using a previously reported method (Scheme 1) [33]. 2-Chloropropionyl chloride reacted with the hydroxyl groups of PEG to generate initiation sites for SET-LRP. Then NIPAM monomers were grafted on both sides of PEG-1 and polymerized in situ with initiation by the 2-chloro group. If all the NIPAM molecules are polymerized, the resulting polymerization degree of NIPAM at each side is 25.

The structure of the PEG-PNIPAM block copolymer was determined using ^{1}H NMR spectroscopy (Fig. 1(a)). All the proton chemical shifts matched those in the PNIPAM block well. The characteristic chemical shifts of the PNIPAM block were clearly observed at 6.4 (4), 4.01 (2), and 1.18 (1) ppm, from N–H, –CH–, and $–CH_3$, respectively [33,35]. The chemical shift of the methylene proton of PEG (3) was observed at 3.63 ppm. A comparison of the areas of the methylene proton peak of PEG (3.63 ppm) and the methine proton peak of PNIPAM (4.01 ppm) shows that the polymerization degree of PNIPAM was 50, i.e., 25 for each initiation site. The polymerization degree is in good agreement with the reagent ratio. GPC analysis of the PEG-PNIPAM composite showed that the polymerization process was well controlled (Fig. 1(b)). GPC analysis of PEG-PNIPAM in THF gave an $M_{n,GPC}$ of 7841 and a polydispersity index [weight-average molecular mass/M_n) of 1.23. The GPC trace peak was sharp and symmetric, confirming well-controlled polymerization. No tailing or shoulders at the lower- or higher-molecular-mass side were observed, indicating that only one type of product was obtained. The $M_{n,NMR}$ was 7763, which is very close to $M_{n,GPC}$. The presence of PNIPAM in the PEG-PNIPAM polymer was further confirmed by FTIR (Fig. 1(c)). The peaks at 1547 (N–H) and 1649 (C=O) cm^{-1} confirmed that PNIPAM was successfully grafted on PEG [21-22].



Scheme 1. Synthesis of linear PEG-PNIPAM copolymer.

3.2. Loading of sub-2-nm Pd nanoclusters on thermoresponsive PEG-PNIPAM polymer

A simple method was used to load Pd nanoclusters on the PEG-PNIPAM copolymer to form a Pd/PEG-PNIPAM composite. When the block copolymer was added to $PdCl_2$ aqueous solution, Pd^{2+} bonded to the NH groups of the PEG-PNIPAM polymer via electrostatic interactions. The NH_2 groups then acted as reducing sites, and Pd^{2+} was reduced to Pd^0 by the surrounding NH_2 groups [36,37]. The color of the reaction mixture turned from bright yellow to light brown after a few minutes, indicating the formation of Pd nanoclusters. ICP-AES showed that the Pd loading on the composite was 4.4 wt%.

Fig. 2 shows a TEM image of the Pd/PEG-PNIPAM composite and a high-resolution TEM (HRTEM) image of the Pd clusters. The TEM image shows a thin sheet of PEG-PNIPAM. Ultra-small Pd clusters are densely loaded on the polymer. The Pd diameters calculated from Fig. 2(b) and 2(c) are around 2 nm. The HRTEM image in Fig. 2(c) shows a lattice spacing of 0.224 nm, corresponding to the (110) plane of Pd. The oxidation state of Pd in the Pd/PEG-PNIPAM composite was determined using

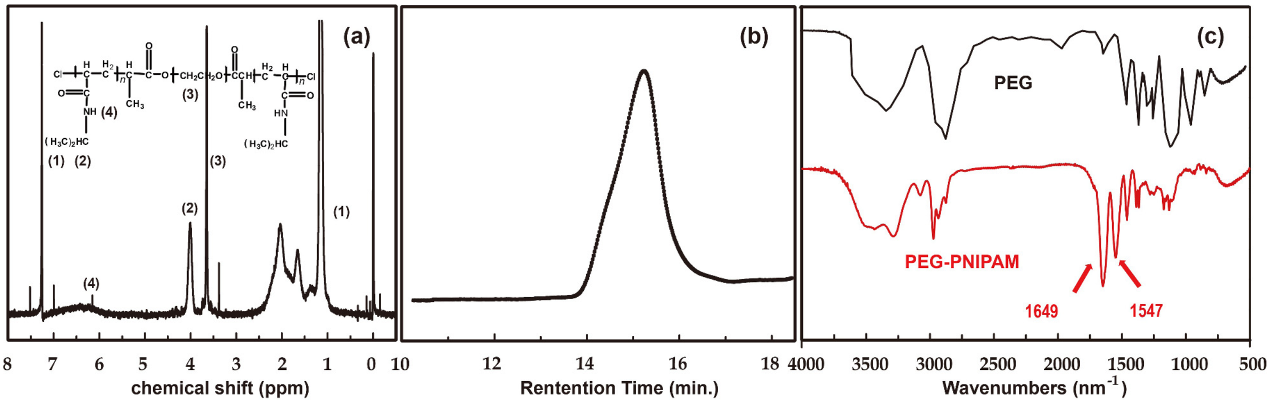


Fig. 1. (a) ^{1}H NMR spectrum of PEG-PNIPAM in $CDCl_3$, (b) GPC trace for PEG-PNIPAM, and (c) FTIR spectra of PEG and PEG-PNIPAM polymers.

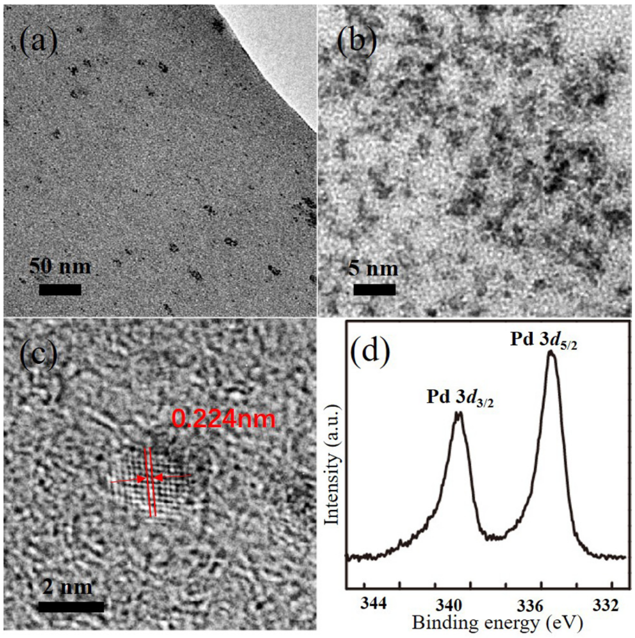


Fig. 2. (a) and (b) TEM images of Pd/PEG-PNIPAM composite at different magnifications, (c) HRTEM image of Pd nanoclusters, and (d) XPS profile of Pd in Pd/PEG-PNIPAM composite.

XPS; the binding energy of 340.5 eV shows that Pd^{2+} was successfully reduced to metallic Pd^0 by PEG-PNIPAM (Fig. 2(d)).

The phase transition of PNIPAM is affected by its molecular mass and concentrations of other polymers [38]. Studies have shown that the PEG content greatly affects the phase-transition behavior of PNIPAM-*g*-PEG [39]. The LCST of PNIPAM in aqueous solution is typically 32 °C [40]. Fig. 3 shows the temperature dependence of the optical transmittance at 500 nm for 1 g/L aqueous suspension of Pd/PEG-PNIPAM. The solution temperature was kept at 30 °C, and then increased to 50 °C at a rate of 1 °C/min. The light-brown clear solution at 30 °C, which had a transmittance of nearly 70%, became cloudy and the transmittance decreased to about 3% at 45 °C. The LCST of this composite was determined to be about 41 °C. The inset in Fig. 3 shows digital images of the sample at 30 and 50 °C. When the cloudy suspension was cooled to room temperature, it became transparent again. The phase transition provides strong evidence of PEG-PNIPAM formation. This transition enables the catalyst to be recycled easily.

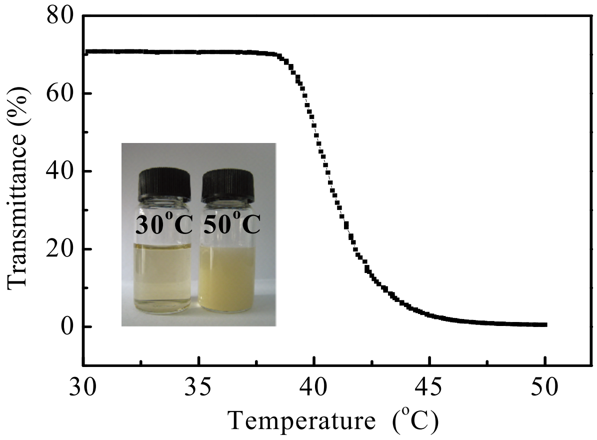


Fig. 3. Temperature dependence of optical transmittance at 500 nm for 1 g/L aqueous suspension of Pd/PEG-PNIPAM.

Although this phase transformation was observed in aqueous solution, we believed that the thermo-responsive ability of PNIPAM would also be useful in catalysis in organic solutions. In this work, the activity of the catalyst in Suzuki reactions performed in a mixed water/ethanol solution was studied. We hypothesized that above the LCST, a hydrophobic nanoenvironment would be formed in the solution, and this nanoenvironment would be enriched with hydrophobic guest molecules (such as iodobenzene or phenylboronic acid in our catalytic reaction) in water. Nanoreactor enrichment would greatly accelerate the reaction, as shown in other studies [18,41].

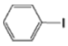
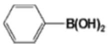
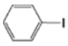
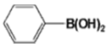
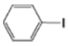
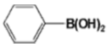
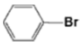
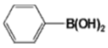
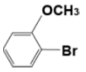
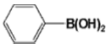
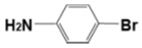
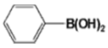
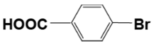
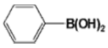
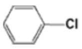
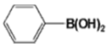
3.3. *Catalytic performance of Pd/PEG-PNIPAM composite*

We performed Suzuki cross-coupling reactions as model reactions to evaluate the catalytic ability of the composite nanoreactor. The iodobenzene substituents were varied to test the effects of substitution. The results for Suzuki reactions performed using various reagents are listed in Table 1. The results show that the composite showed excellent activity in all these reactions. When iodobenzene was used, only the cross-coupling product biphenyl was detected by HPLC and GC; no other byproducts were produced. The yield of biphenyl reached 100% in 10 s (Table 1, run 1), with a TOF of 4.3×10^4 h^{-1}. When the reagent/catalyst ratio was increased from 120 to 1600, 100% yields were reached in 3 min, with a TOF of 3.2×10^4 h^{-1} (Table 1, run 3). This high activity is remarkable for heterogeneous catalysis, and shows the advantage of using PEG-PNIPAM as a catalyst support. A commercial Pd/C was used as the catalyst for comparison, and 30 min was needed to reach 100% conversion under the same reaction conditions as in Table 1, run 1. When bromobenzenes with different substituents were used, all the bromobenzenes showed high reactivity. The product yields were 80–100% in 3 min (Table 1, runs 4–7). Even chlorobenzene showed excellent reactivity over this Pd/PEG-PNIPAM catalyst, giving a 65% product yield in 5 min at 80 °C (Table 1, run 8). These results show that the composite is extremely active in Pd-catalyzed C–C cross-coupling reactions.

When the Pd/PEG-PNIPAM was used in three consecutive runs, the catalyst showed significant deactivation. The iodobenzene conversion decreased to 5% in 10 s after three consecutive runs. A TEM image of the used composite showed that the Pd nanoclusters aggregated into large particles of size several hundred nanometers. Because of their high surface energy, the sub-2 nm Pd nanoparticles have a high tendency to aggregate, and the interactions between PNIPAM and Pd are not sufficient to anchor the Pd nanoparticles. Prevention of aggregation of the sub-2-nm Pd nanoparticles in Pd/PEG-PNIPAM could enable their activity to be maintained. In future work, stabilizing methods such as combination with silica or other porous polymers or silica that have stronger affinities with Pd will be studied. However, these large Pd particles can be easily recovered by centrifugation. ICP-AES analysis detected only a

Table 1

Suzuki cross-coupling reactions catalyzed by Pd/PEG-PNIPAM[a].

Run	Reagent 1	Reagent 2	T/°C	Time	Yield	TOF (h^{-1})
1			80	10 s	100%	4.3×10^4
2			25	1 min	100%	7.2×10^3
3 [b]			80	3 min	100%	3.2×10^4
4			80	3 min	100%	2.4×10^3
5			80	3 min	90%	2.16×10^3
6			80	3 min	80%	1.92×10^3
7			80	3 min	96%	2.3×10^3
8			80	5 min	65%	936

[a] Reaction condition: 80 °C, 0.15 mmol iodobenzene, 0.3 mmol phenylboronic acid, 0.3 mmol K_2CO_3, 0.15 mmol pentamethylbenzene and 3 mg catalyst were added to 3 mL ethanol and 3 mL H_2O mixture. Reagent/catalyst ratio was 120.

[b] reagent/catalyst ratio was 1600.

trace of Pd in the reaction solution, showing that almost all the Pd nanoparticles were loaded on the PEG-PNIPAM rather than leaching into the reaction system. The recovered Pd nanoparticles can therefore be recycled to regenerate the Pd catalyst. Although Pd/PEG-PNIPAM was only active in the first run, it has good potential for practical applications because of its extremely high catalytic activity and convenient recycling.

4. Conclusions

A PEG-PNIPAM copolymer was synthesized as a support for Pd nanoclusters. The PEG-PNIPAM chains acted as both reducing agents and catalyst supports. In Suzuki reactions using this Pd/PEG-PNIPAM catalyst, the environment around Pd/PEG-PNIPAM was enriched with both hydrophilic and hydrophobic reactants, and therefore the catalyst showed excellent activity. The reaction with iodobenzene and phenylboronic acid was completed in 10 s, with a TOF value of 4.3×10^4 h^{-1}. The reaction with chlorobenzene gave 65% conversion in 5 min. The Pd/PEG-PNIPAM can be easily recycled because of the reversible phase transition of PNIPAM.

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Graphical Abstract

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Simple synthesis of sub-nanometer Pd clusters: High catalytic activity of Pd/PEG-PNIPAM in Suzuki reaction

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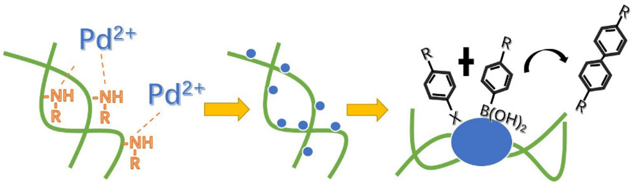
A temperature-responsive copolymer, i.e., PEG-PNIPAM, was synthesized and stabilized ultra-small Pd clusters were formed on it by direct reduction. The sub-2-nm Pd nanoclusters showed outstanding catalytic activities in Suzuki reactions.



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