Carboxymethylcellulose-supported Palladium Nanoparticles Formed \textit{in situ} for Suzuki-Miyaura Coupling Reaction

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Abstract
A green experiment is described here for direct fabrication of carboxymethylcellulose-supported palladium nanoparticles (PdNPs@CMC) in situ through a simple self-assembly and self-reduction process between carboxymethylcellulose (CMC−Na) and PdCl₂ solution. The PdNPs@CMC was well characterized by ICP, UV-Vis, XPS, FTIR, SEM, and TEM techniques. The in situ synthesized PdNPs@CMC was proved to be an efficient catalyst for Suzuki–Miyaura coupling reaction under mild aerobic conditions. The superior catalytic performance of PdNPs@CMC is attributed to the coordination with carboxyl groups (−COO⁻) and free hydroxyl groups (−OH) as well as polymeric capping effect of CMC. Moreover, the catalyst showed no significant loss of its activity at least three consecutive cycles. This laboratory class is involved in the preparation and characterization of PdNPs@CMC as well as its catalytic application in Suzuki–Miyaura cross coupling reaction under green conditions. This laboratory class is suggested to divide into two parts. The first part includes the fabrication of catalyst in situ through a self-assemble and self-reduction of Pd(II) with CMC−Na, and characterization of the as-prepared catalyst using various techniques. The second part employs the resulting catalyst to perform a microscale Suzuki-Miyaura reaction, recycling of catalyst, and characterization of the product. By design, this comprehensive experiment set up for the third-year undergraduate, and aim to make students comprehend the concept of ion-exchange reaction, reduction reaction, carbon-carbon coupling reaction, supported catalysts, nanoparticles, and green chemistry as well as train the fundamental operation capability of students, and improve their experimental skills.

**Keywords:** organic experiment, green chemistry, Suzuki-Miyaura reaction, supported catalyst, palladium nanoparticles, carboxymethylcellulose, upper-division undergraduate, hands-on learning/manipulatives

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1. Introduction

Suzuki–Miyaura cross coupling reaction, i.e., the coupling of aryl halide and arylboronic acid to produce biaryl, is one of the most powerful tools for construction of Csp²−Csp² bond, and has emerged as a hotspot in organic chemistry in recent years [1,2,3]. Due to its high yields, high selectivity, mild condition, and the tolerance of wide scope of functional groups, Suzuki–Miyaura reaction was recognized by the award of the Nobel Prize in Chemistry in 2010 [4]. A considerable number of homogeneous and heterogeneous palladium catalysts have been documented [2,3,5]. Although homogeneous catalysts such as Pd(PPh₃)₄, PdCl₂, Pd(OAc)₂, and Pd–NCH etc. render excellent catalytic performance and selectivity, the application of homogeneous catalysis leads not only tedious operation and recovery of catalyst but also the decomposition of catalysts into Pd black which would reduce catalytic activity and contaminate the product [5]. To overcome these deficiencies, supported palladium nanoparticles (Pd NPs) have fascinated considerable interest because the ligands tethered on the support can efficiently control the formation of Pd NPs and further prevent their agglomeration [6]. In recent years, a plenty of articles have been published to development of retrievable supported Pd NPs catalysts using a variety of organic or inorganic materials, such as polymers or biopolymers, magnetic materials, metal organic framework (MOF) and so on [5,7,9]. The catalytic performance of Pd NPs depends on the particle size and dispersion of the active sites, while the reusability and catalytic lifespan associate with their stability against agglomeration. In general, the stable Pd NPs can be obtained by using suitable ligands or supporting matrix. A current challenge in this area is the development of feasible synthetic strategy that could simultaneously achieve the target of highly catalytic activity, and facilitate recovering and recycling of catalyst.

Sodium carboxymethylcellulose (CMC−Na) [10], one of the most important biodegradable water-soluble derivatives of naturally abundant cellulose, bears an abundance of carboxylate (−COO⁻) and inherent hydroxyl (−OH) groups on its cellulosic chain, which makes it a practical support to immobilize Pd NPs via the interaction of coordinated bonds between the counter Pd NPs species and CMC support. Based on its properties, carboxymethylcellulose-supported Pd NPs (PdNPs@CMC) can be achieved via the assembled complexation between −COO⁻ and Pd²⁺ through the ion-exchange reaction, which is further reduced in situ to PdNPs@CMC by means of the reductivity of CMC−Na itself. Then the as-prepared PdNPs@CMC catalyst was characterized in detailed by various methods such as UV-Vis, FT-IR, SEM, TEM, EDX and XPS before employed for catalyzing Suzuki-Miyaura cross-coupling reaction (Figure 1). In the same way, the reaction products were identified by ¹H NMR and ¹³C NMR and compared with the data reported in literatures.

![Figure 1. Suzuki-Miyaura coupling reaction catalyzed by PdNPs@CMC](image-url)
To date, the Suzuki-Miyaura reaction has been the subject of several published undergraduate laboratory experiments that have focused on various aspects of organic chemistry [11,12]. However, most of them are carried out in homogeneous catalysts. Very few of them are involved for employing supported Pd NPs catalyst for Suzuki–Miyaura reaction. Herein this novel experiment was designed to provide an excellent learning experience for upper-division undergraduate students as it provides sophisticated research strategies and methodologies.

Pedagogically, this two-day-long experiment was successfully implemented in a third-year undergraduate organic chemistry laboratory program in 2019. All the synthetic procedures are straightforward and avoid using high-toxic reagents in which all are easily accessible and inexpensive, and obtain high yield in the one-step Suzuki–Miyaura cross-coupling reaction, from which students could gain the knowledge of organic synthesis, nanocatalysis, and green chemistry. In the laboratory, students simultaneously individually exert a series of microscale operation to prepare PdNPs@CMC catalyst and perform Suzuki–Miyaura reaction.

2. Pedagogical Significance

The key pedagogical goals this experiment focus on: (i) applying fundamental theory presented in the classroom to laboratory which are tested experimentally, (ii) employing microscale operations to prepare PdNPs@CMC catalyst and using it as a catalyst to exert Suzuki–Miyaura cross-coupling reaction, (iii) adopting instrumental analysis for both of PdNPs@CMC catalyst and biaryl product. As learning outcomes, students will be able to (i) comprehend the concept of ion-exchange reaction, reduction reaction, carbon-carbon coupling reaction, supported catalysts, nanoparticles, and green chemistry; (ii) understand the important aspect of nanopalladiun-catalyzed Suzuki–Miyaura reaction; (iii) further cognition towards the structure and properties of polysaccharide derivatives such as carboxymethylcellulose with multifunctional groups such as hydroxyl (−OH), carboxylate (−COO); (iv) be familiar with the necessary experimental operations and instrumental analysis.

The achievement of these goals is primarily assessed quantitatively by evaluation of the laboratory reports presented by students after the experiments. The laboratory reports must include introduction, experimental section, results and discussion, and conclusion. In introduction section, the pedagogical goals and importance of this experiments is simply described. In the experimental section, details of the preparative procedure of catalyst, characterization of catalyst, detailed procedure of perform Suzuki–Miyaura cross-coupling, recycling of catalyst, isolation of product, calculated the yield, and characterization of biaryl product are essential. In the results and discussion section, the students must focus on discussion of the roles of the Pd(0), the boronic acid, the base, and water. Especially, center on discussion of why the Pd(0) can efficient initiate Suzuki–Miyaura reaction. And must discuss the as-prepared PdNPs@CMC catalyst is a nanocatalyst by means of various analysis. In conclusion section, the results obtained from the experiment must be concise and to the point.

3. Experimental Procedures

There were five students doing this this comprehensive experiment in a laboratory course, and each one student was assigned to carry out all the experiments independently according to their student ID. The total class hours of this experiment were 24 h (3 days a week, 8 class hours per day, 60 mins per class hour), and all the students would continuously conduct the experiments during these periods.

3.1. Materials and Apparatus

All chemicals and solvents were analytical grade and were used as received without further treatment. Melting point was measured on an Electrothermal X6 microscopic digital melting point apparatus. The elemental palladium content of the catalyst was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using Perkin-Elmer Optima 20000V instrument. UV-Vis-near infrared spectrophotometer were operated on Hitachi UH4150. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Shimadzu Amicus X-ray photoelectron spectrometer with an Al Kα excitation. Flourier transform infrared spectra (FTIR) were collected on a Nicolet6700 spectrophotometer in KBr pellet within the spectral range of 4000-400 cm⁻¹ at 2 cm⁻¹ resolution and 32 scans. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) were conducted with a Philips XL 30E instrument. Transmission electron microscopy (TEM) was performed with a JEM-100C instrument operating at 40-100 kV. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker-300 Avance Spectrometer with CDCl₃ as solvent using TMS as an internal standard at 300 MHz and 75 MHz, respectively.

The required chemicals and characterization sections are described in the Supporting Information.

3.2. The Preparation of PdNPs@CMC
(1st Section of First Laboratory Class, 8h)

PdCl₂ (0.2 g) and distilled water (2 mL) were charged into a 25 mL round-bottom flask, then two drops of 1 mol/L HCl was added into the mixture to promote the dissolution of PdCl₂. The resultant PdCl₂ solution was added dropwise with 1% CMC−Na (4 mL) at room temperature with continuous gentle stirring to form CMC-Pd(II) complex via ion exchange reaction. Subsequently, the mixture was added with 1 mol/L NaOH solution to adjust pH to 6 and then heated at 80°C in oil bath for around 30 min till the mixture turned to dark which visually indicates the formation of Pd(0) via the self-reduction of Pd(II) by CMC−Na. The resulting black suspension was collected from the mixture by suction and washed thoroughly with distilled water till the filtrate became colorless and neutral, then dried in vacuum to constant weight to provide the PdNPs@CMC as black powders. The preparation is present in Figure 2.
In this section, the students were trained to prepare the PdNPs@CMC catalyst using CMC–Na as a cation exchanger, self-assemble template, a reductant, and a catalyst support. Especially, the synthesis of PdNPs@CMC has a significant color change, which students may be found interesting.

3.3. The Characterization of PdNPs@CMC
(2nd Section of First Laboratory Class, 8h)

The as-prepared PdNPs@CMC catalyst was characterized by various techniques such as ICP, UV-vis, XPS, FTIR, SEM, EDX, and TEM. These characterizations need the students work individually on corresponding instruments under the assistance of technicians. Varied experiment times were depended on different individuals, but the total experiment time of this section was about 6-8 h.

In this section, the student learned to use comprehensive instrumental analysis to characterize the catalyst in organic chemistry research.

3.4. Suzuki–Miyaura Coupling Reaction
Catalyzed by PdNPs@CMC (1st Section of the Second Laboratory Class, 4h)

$p$-Iodoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), $K_2CO_3$ (2 mmol), catalytic amount of PdNPs@CMC (0.5 mol% of Pd) were charged into 75% ethanol (5 mL) in Schlenk tube, then the reaction mixture was heated with stirring at refluxing for a specific time, along with TLC for the progress tracking. The reaction finished less than 30 min and ethyl acetate was added to the flask and the catalyst was removed by suction, washed with ethyl acetate adequately, and dried in air for the next run. The organic phase was washed with brine and dried over anhydrous Na$_2$SO$_4$. The crude product was obtained after removal of the organic solution using a rotary evaporator. The desired pure products were further purified by recrystallization with ethanol. The experimental procedure is shown in Figure 3. The product is known and confirmed by $^1$H NMR and $^{13}$C NMR, which data were found to be identical to those reported in the literature.
The goals in this section for students (i) were familiar with the microscale experimental operation and apparatus used in Suzuki–Miyaura reaction, including setting up the apparatus, monitoring the reaction progress by means of TLC, working up on reaction mixture, purification of product with recrystallization, and confirmation of the final product with NMR. (ii) to get the knowledge of the fundamentals of the mechanism of Pd-catalyzed Suzuki–Miyaura reaction, including oxidative addition, transmetalation, and reductive elimination.

3.5. The Recycling Experiments of PdNPs@CMC (2nd Section of the Second Laboratory Class, 4h)

The recovered of PdNPs@CMC was used directly without further treatment and the experimental procedure is similar with that mentioned above.

In this section, the students could understand the recycling of supported catalysts.

3.6. Hazards

Gloves, goggles, lab coats, and masks should be worn throughout the whole experiment, avoiding the direct contact of the reagents with skin or inhalation of vapors. All the chemicals are of common use in the organic laboratory. Hydrochloric acid would cause corrosion to the skin or organization, its vapor could lead to eye irritation and respiratory tract damage. Stock solutions of 1 mol/L hydrochloric acid should be prepared in a fume hood. Sodium hydroxide is corrosive and irritant if touched by skin, and it may cause burn when dissolved in water which releases out heat. Phenylboronic acid is toxic if swallowed and causes irritation. p-Iodoanisole is irritating to eyes, respiratory system, and skin. phenylboronic acid may be harmful if inhaled, swallowed, or absorbed through skin. Ethanol, n-hexane, and ethyl acetate etc. organic liquids should be handled in a well-ventilated fume hood. Palladium chloride is of high toxicity if swallowed and may cause allergic skin reaction. Sodium carboxymethylcellulose is not considered toxic, but care should be taken to avoid inhalation. CDCl₃ is toxic and a cancer suspect agent. The biaryl product is not considered harmful, but caution should be taken to avoid inhalation or contact with skin. Other inorganic salts such as sodium chloride, and anhydrate sodium sulphate are low toxic. The reaction involves heating steps which may cause skin burned if handled incorrectly.

4. Results and Discussion

4.1. Synthesis and Characterization of PdNPs@CMC

The PdNPs@CMC was prepared directly from PdCl₂ and CMC–Na solution via metathetical and reductive reactions in a one-step one-pot reaction. It should be pointed out here that the visually color change was noted in the reaction mixture of PdCl₂ and CMC–Na solution. The color of the solution changed from initially brown to dark, implying the formation of elemental PdNPs in the solution. After separation and drying of PdNPs@CMC to constant weight, the Pd loading was determined to be 4.42 mmol/g by ICP analysis.

The formation of PdNPs was confirmed by UV-visible spectroscopy in the range of 200-800 nm (Figure 4). The absorption spectra of CMC (curve a) and PdCl₂ solution (curve b) were used for references. As can be seen from Figure 4, no absorption spectra of CMC–Na were shown in curve (a). In curve (b), the absorption bands located at 222 and 276 nm were assigned to the charge-transfer transition between Pd(II) and Cl⁻. In curve (c), the disappearance of these two peaks of PdCl₂ suggested the reduction of the Pd(II) cations.

Figure 4. UV-vis spectra of CMC–Na aqueous solution (a), PdCl₂ aqueous solution (b), and PdNPs formed in situ from CMC and PdCl₂ aqueous solution (c)

XPS can confirm the oxidation state of palladium. As we can see from Figure 5, the binding energy of Pd 3d in the as-synthesized catalyst is 335.58 and 340.83eV respectively, which is consistent with that in Pd(0), proving the palladium of PdNPs@CMC is in zero-valent state.

Figure 5. XPS spectrum of Pd3d in the PdNPs@CMC

The FTIR of CMC–Na (curve a), CMC–Pd(II) (curve b), and PdNPs@CMC (curve c) in the range of 4000-500 cm⁻¹ were shown in Figure 6. The characteristic peaks located at 1619 cm⁻¹, and 1421 cm⁻¹ in curve (a) are
assigned for carboxylate (−COO\(^−\)) asymmetric and symmetric stretching vibration. As can be seen from curve (b) and curve (c), these two distinct peaks negatively shifted to 1610 cm\(^−1\) and 1407 cm\(^−1\) in curve (b), and 1594 cm\(^−1\) and 1406 cm\(^−1\) in curve (c), implying the interaction of −COO\(^−\) groups with Pd\(^{2+}\) and Pd(0), respectively.

As is known to all, the surface morphology of catalysts is of great impact on its catalytic activity, so the as-synthesized PdNPs@CMC was characterized by SEM (Figure 7). The SEM image shows that the PdNPs@CMC was made up of microparticles with rough surface, facilitating better mass transfer process which is propitious to improving its catalytic activity. In the meantime, the existence of carbon, oxygen and palladium in the PdNPs@CMC was confirmed by EDX (Figure 8) associated with SEM analysis. As a result, it is reasonable to assume that Pd has been successfully loaded on CMC.

In order to determine the size and morphology of PdNPs@CMC, TEM analysis was performed (Figure 9). The TEM image reveals that as-prepared PdNPs are formed by the accretion of the tiny particles and finally gain the size around 100 nm.
4.2. Performance of Suzuki–Miyaura Cross Coupling and Recycling of PdNPs@CMC Catalyst

Initially, the plausible mechanism of the Suzuki-Miyaura cross-coupling reaction was provided to students to discuss before the beginning of experiments. The mechanism of the Suzuki–Miyaura reaction catalyzed by palladium-based catalysts is shown in Figure 10. The general steps include oxidative addition, transmetalation, and reductive elimination [12]. In the catalytic cycle, the base plays multiple roles of facilitating transmetalation and formation of borate salts, thus the dose of base must be excessed.

To certify that the resultant PdNPs@CMC can be of practical use in Suzuki–Miyaura cross coupling, the students perform the typical experiment with p-iodoanisole and phenylboronic acid (Figure 1) using the PdNPs@CMC catalyst prepared by themselves along with characterization of the product by $^1$H NMR and $^{13}$C NMR (see Supporting Information for detailed spectrum).

The reusability of catalyst is a very important factor in catalysis. In order to clarify this issue, catalytic recycling experiments were performed using the reaction of p-iodoanisole and phenylboronic acid. After completion of the reaction, the catalyst could be conveniently and efficiently recovered from the reaction mixture by suction and can be used in the next run directly. The results showed that this catalyst can be reused without losing its activities for at least three cycles.

5. Conclusion

This creative experimental design of carboxymethylcellulose-supported nanopalladium catalyst (PdNPs@CMC) was successfully performed by third-year undergraduate students in a facile and green way. Pd(II) was first bonded to the carboxymethylcellulose by ion-exchange to form CMC–Pd$^{II}$, which was further greenerly reduced in situ to PdNPs@CMC simply by CMC itself. The carboxyl and hydroxyl groups in CMC coordinated with PdNPs to form PdNPs@CMC with stable structures, which can efficiently catalyze Suzuki–Miyaura coupling, an important reaction in organic synthesis for C–C bond formation. The catalyst and product were confirmed by various characteristic techniques, which indicate that the catalyst could be prepared easily in short time with superior catalytic activity along with obvious experimental phenomena during process, and the product of coupling reaction is of excellent yield. The whole design for catalyst synthesis and its catalyzed reaction in an environmentally friendly method are consistent with the aim of enhancing the theoretic and experimental operation level of students, which is perfect for undergraduate innovative experiment training.

Supporting Information

The Supporting Information can be seen and downloaded from our homepage https://www.uni-saarland.de/lehrstuhl/kay/ag-didaktik/downloads/.

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Supporting Information

1. Experimental

1.1. Reagents and Apparatus

Table S1. Reagents used in the experiments

| Reagents             | Specifications | Manufacturers                                           | Abbreviation or molecular formula |
|----------------------|---------------|---------------------------------------------------------|-----------------------------------|
| Palladium chloride   | 59-60%        | Shanghai Meyer Chemical Technology Co., Ltd. (China)     | PdCl₂                             |
| Carboxymethylcellulose Sodium | AR       | Shanghai Macklin Biochemical Co., Ltd. (China)          | CMC–Na                            |
| Hydrochloric acid    | 36-38%        | Guangzhou Chemical Reagent Factory (China)               | HCl                               |
| Sodium hydroxide     | 97%           | Shenzhen Dieckmann Technology Development Co., Ltd. (China) | NaOH                              |
| p-Iodoanisole        | 98%           | Shanghai Meyer Chemical Technology Co., Ltd. (China)     | C₆H₅I                             |
| Phenylboronic acid   | 97%           | Shanghai Macklin Biochemical Co., Ltd. (China)           | PhB(OH)₃                          |
| potassium carbonate anhydrous | AR     | Tianjin Damao Chemical Reagent Factory (China)           | K₂CO₃                             |
| n-hexane             | AR            | Guangdong Guanghua Sci-Tech Co., Ltd. (China)            |                                  |
| Sodium chloride      | AR            | Tianjin Damao Chemical Reagent Factory (China)           | NaCl                              |
| Ethyl acetate        | AR            | Guangdong Guanghua Sci-Tech Co., Ltd. (China)            | EA                                |
| Sodium sulphate anhydrous | AR       | Tianjin Damao Chemical Reagent Factory (China)           | Na₂SO₄                            |
| Absolute ethanol     | AR            | Guangdong Guanghua Sci-Tech Co., Ltd. (China)            | EtOH                              |

Table S2. Preparation procedures of solution

| Solution    | Specifications | Procedures                                                                 |
|-------------|----------------|-----------------------------------------------------------------------------|
| HCl         | 1mol/L         | Withdraw 83.3 mL concentrated hydrochloric acid and dilute it with distilled water to a volume of 1 L in volumetric flask |
| NaOH        | 1mol/L         | Add 40 g solid base of NaOH to a beaker, dissolve it with moderate distilled water then transfer to 1 L volumetric flask for constant volume |
| NaCl        | Saturated      | Add excessive NaCl to distilled water with thorough stirring, then stand for a while and extract its supernatant |
| Ethanol     | 75%            | Add 131.5 mL distilled water to 500 mL absolute ethanol with thorough stirring |

Table S3. Apparatus used in the experimental equipment

| Apparatus                | Model       | Manufacturers                                                      |
|--------------------------|-------------|-------------------------------------------------------------------|
| Magnetic heating plate   | 524G        | Shanghai Meiyingpu Instrument Manufacturing Co., Ltd. (China)      |
| Circulating water vacuum pump | A-1000s    | Shanghai EYELA Instrument Co., Ltd. (China)                        |
| Rotary evaporator        | N-1300      | Shanghai EYELA Instrument Co., Ltd. (China)                        |
| TLC analyzer             | ZF-6        | Shanghai Jiapeng Technology Co., Ltd. (China)                     |
| Electric blast drying oven | DGX-9053BC-1 | Shanghai Fuma Laboratory Instrument Co., Ltd. (China)             |
Table S4. Instruments for characterization

| Instruments | Model       | Manufacturers                        | Notes                                           |
|-------------|-------------|--------------------------------------|-------------------------------------------------|
| Nuclear Magnetic Resonance Spectrometer (NMR) | Bruker Advance 300MHz | Bruker Corporation (USA) | CDCl₃ for solution and TMS as internal standard |
| Micro melting point instrument (m.p.) | X6 | Beijing Zhongyiboteng-Tech. Co., Ltd. (China) |                                             |
| Fourier infrared spectrometer (FTIR) | Nicolet 6700 | Thermo Fisher Scientific Inc. (USA) | Compression with KBr                             |
| Inductive coupled plasma atomic emission spectrometer (ICP-AES) | Optima 20000V | PerkinElmer Inc. (USA) | With CuKa radiation, 40kV for voltage and 40mA for current |
| X-ray photoelectron spectroscopy (XPS) | Shimadzu Amicus | Shimadzu Corporation (Japan) |                                             |
| Transmission electron microscopy (TEM) | JEM-100C | JEOL Ltd. (Japan) |                                             |
| Scanning electron microscopy (SEM) | Philips XL 30E | Royal Philips Electronics (Netherlands) |                                             |
| energy-dispersive X-ray (EDX) | Philips XL 30E | Royal Philips Electronics (Netherlands) |                                             |
| UV-Vis-near infrared spectrophotometer (UV-Vis) | Hitachi UH4150 | Hitachi Ltd. (Japan) |                                             |

1.2. The Preparation of PdNPs@CMC Catalyst

PdCl₂ (0.2g) and distilled water (2 mL) were charged into a 25 mL round-bottom flask, then two drops of 1mol/L HCl was added into the mixture to promote the dissolution of PdCl₂. The resultant PdCl₂ solution was added dropwise with 1% CMC−Na (4 mL) at room temperature with continuous gentle stirring to form CMC−Pd(II) complex via ion exchange reaction. Subsequently, the mixture was added with 1 mol/L NaOH solution to adjust pH to 6 and then heated at 80°C in oil bath for around 30 min till the mixture turned to dark which visually indicates the formation of Pd(0) via the self-reduction of Pd(II) by CMC. The resulting black suspension was collected from the mixture by suction and washed thoroughly with distilled water till the filtrate became colorless and neutral, then dried in vacuum to constant weight to provide the PdNPs@CMC as black powders.

1.3. Suzuki-Miyaura Coupling Reaction Catalyzed by PdNPs@CMC and Recycling of Catalyst

p-Iodoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ (2 mmol), catalytic amount of Pd⁰NPs@CMC (0.5 mol% of Pd) were charged into 75% ethanol (5 mL) in Schlenk tube, then the reaction mixture was heated with stirring at refluxing for a specific time, along with TLC for the progress tracking. The reaction finished less than 30 minutes and ethyl acetate was added to the flask and the catalyst was removed by suction, washed with ethyl acetate adequately, and dried in air for the next run. The organic phase was washed with brine and dried over anhydrous Na₂SO₄. The crude product was obtained after removal of the organic solution using a rotary evaporator. The desired pure products were further purified by recrystallization with ethanol. The product is known and confirmed by FTIR, ¹H NMR and ¹³C NMR, which data were found to be identical to those reported in the literature.

The recovered of PdNPs@CMC was used directly without further treatment and the experimental procedure is similar with that mentioned above.
1.4. Characterization of the Product

4-Methoxybiphenyl. Yield: 90%, mp(°C): 86.9-89.1. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.58 – 7.50 (m, 4H, Ar-H), 7.41 (m, 2H, Ar-H), 7.36 – 7.21 (m, 1H, Ar-H), 6.98 (d, $J = 8.7$ Hz, 2H, Ar-H), 3.85 (s, 3H, CH$_3$O). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 159.14 , 140.83 , 133.78 , 128.73 , 128.16 , 126.75 , 126.66 , 114.20 , 55.36.

$^1$H NMR spectra

Figure S1. $^1$H NMR spectrum (300 MHz) of 4-methoxybiphenyl in CDCl$_3$
Figure S2. $^{13}$C NMR spectrum (75 MHz) of 4-methoxybiphenyl in CDCl₃

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