

# Photocatalytic Suzuki Coupling Reaction Using Conjugated Microporous Polymer with Immobilized Palladium Nanoparticles under Visible Light

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Supporting Information

irst discovered in the late 1970s, palladium (Pd)-catalyzed Suzuki cross-coupling reaction is one of the most powerful one-step pathways for the formation of carbon-carbon bonds in organic synthesis.<sup>1,2</sup> Typically, Suzuki coupling reactions are performed under homogeneous conditions using a variety of phosphine ligand/palladium catalytic complexes.<sup>3-5</sup> Despite the relatively high efficiency of these homogeneous systems, the recovery of the costly and potentially toxic palladium catalysts remains as a pressing issue in the development toward a greener, more sustainable chemical industry. Heterogeneous catalysts are favored over homogeneous catalysts because of their facile recyclability and easy compatibility with continuous flow systems.<sup>6–11</sup> Extensive research has been done to develop heterogeneous Pd catalysts for Suzuki coupling reactions, such as the immobilization or stabilization of Pd nanoparticles (NPs) on silica,<sup>13–15</sup> carbon nanotubes,<sup>16</sup> polymers,<sup>17–19</sup> metal oxides,<sup>20,21</sup> dendrimers,<sup>22,23</sup> and graphene layers.<sup>24</sup> However, due to the high activation barrier of substrates associated with the rate-limiting steps, the majority of these systems with heterogeneous catalysts require elevated temperature (≥100 °C or under reflux conditions), intensive heating, and prolonged reaction time, which may lead to undesired side reactions and compromise the stability of the catalysts.<sup>12,25</sup>

Sunlight is a clean, abundant, and sustainable source of energy, and the visible light range of the spectrum accounts for 44% of the total solar energy as opposed to only 3% from the ultraviolet (UV) light.<sup>26</sup> Current research in the field of heterogeneous visible light photocatalysis is predominantly focused on the photoredox reactions<sup>27</sup> such as the oxidation of alcohols and amines or the hydroxylation of aromatic compounds,<sup>28,29</sup> C–H activation reaction,<sup>30</sup> hydrogen generation,<sup>31</sup> and oxygen activation,<sup>32</sup> whereas there have been very few reports on classic cross-coupling reactions, such as Suzuki coupling reactions. Recently, Wang et al. reported the harvesting of visible light with plasmonic Au-Pd nanostructures and their use as photocatalysts for Suzuki coupling reactions.<sup>33</sup> Zhu et al. demonstrated also that Au-Pd alloy NPs can strongly absorb visible light and efficiently catalyze several cross-coupling reactions at ambient temperature.<sup>34-36</sup> Apart from plasmonic metals, Li et al. reported that mesoporous g-C<sub>3</sub>N<sub>4</sub>, a well-established visible light nonmetal photocatalyst, can be used as photoactive anchoring support for Pd nanoparticles to form a Mott-Schottky heterojunction and increase the electron density surrounding Pd NPs via lightamplified effect.37-40

Conjugated microporous polymers (CMPs), combining semiconductive  $\pi$ -conjugated skeletons with permanent nanopores, have been applied as organic, heterogeneous visible light photocatalysts for a number of photoredox reactions.<sup>41–45</sup> With their broad light absorption and tunable semiconductor-range band gaps, we envision the formation of a hybrid heterojunction, i.e., a metal-semiconductor contact between Pd NPs and CMP, would result in a positively charged region on the CMP and a negatively charged site on the Pd NPs at the interface due to the Schottky effect. Upon photoirradiation, both the average energy and the effective flow of free electrons toward the Pd NPs would be amplified, which can be exploited and harvested to catalyze reactions.

In this work, we aim to utilize the photoamplified heterojunction effect at the interface between a semiconductive conjugated microporous polymer and Pd NPs. We demonstrate the use of conjugated microporous polymer supported Pd NPs (Pd@CMP) as an efficient heterogeneous, visible light photocatalyst for Suzuki coupling at room temperature.

A conjugated microporous poly(benzoxadiazole) network  $(B-BO_3)$  was chosen as the semiconductive polymer support (Figure 1a), on which Pd NPs with sizes between 5 and 10 nm



Figure 1. (a) Polymer backbone structure of B-BO<sub>2</sub>. (b) TEM image of B-BO3 immobilized with Pd NPs with sizes between 5 and 10 nm. (c) UV/vis DR spectra of Pd@B-BO<sub>3</sub> and B-BO<sub>3</sub>. (d) VB (HOMO) and CB (LUMO) band positions of Pd@B-BO<sub>3</sub> and B-BO<sub>3</sub> (vs SCE) measured by cyclic voltammetry.

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were subsequently immobilized, resulting in the hybrid material  $Pd@B-BO_3$  (Figure 1b). To note, the functional groups inside  $B-BO_3$  were end-capped in order to avoid undesired side reactions during the light-induced Suzuki coupling later. About 3 wt % of Pd content in  $Pd@B-BO_3$  was determined via inductively coupled plasma (ICP). The synthetic and characteristic details of the materials are described in the Supporting Information.

The Brunauer-Emmett-Teller (BET) surface area of B-BO<sub>3</sub> was  $612 \text{ m}^2/\text{g}$  with a total pore volume of 0.37 cm<sup>3</sup>/g. The BET surface area of Pd@B-BO<sub>3</sub> was 176  $m^2/g$  with a pore volume of 0.11 cm<sup>3</sup>/g. This is likely due to the weight increase after immobilization with Pd NPs. The pore size of ca. 1.4 nm remained. The UV/vis DR spectrum of Pd@B-BO3 showed a broader absorption than that of B-BO<sub>3</sub> (Figure 1c). This could be attributed to the immobilization of Pd NPs, which also absorb in the visible range due to the interband transition and plasmonic effects. Cyclic voltammetry showed that Pd@B-BO3 exhibited lower valence band (VB) (+1.43 eV vs SCE) and conduction band (CB) (-0.95 eV vs SCE) than B-BO<sub>3</sub> with a VB of +1.35 eV (vs SCE) and CB of -1.08 eV (vs SCE), respectively. The electron paramagnetic resonance (EPR) showed a large increase of the intensity of Pd@B-BO3 in dark and under light irradiation compared to B-BO<sub>3</sub> (Figure S5 in Supporting Information). This could also be caused by the plasmonic effects on the Pd NPs. On the other hand, the intensive signal also indicates a longer living electron-hole pair inside Pd@B-BO3 than in B-BO3.

The coupling of iodobenzene with phenylboronic acid was chosen as a model reaction to study the catalytic activity of  $Pd@B-BO_3$  under visible light irradiation. To avoid the photoheating effect, the reaction vial was submerged in a water bath (Figure S12 in Supporting Information). The screening and control experiments are listed in Table 1. The reaction gave the desired product in an almost quantitative yield at room temperature in 2 h (entry 1). An identical reaction system, which was conducted in dark, resulted only in

Table 1. Screening and Mechanism Study of thePhotocatalytic Suzuki Coupling Reaction Using Pd@B-BO3<sup>a</sup>

х-√	∿_,	$HO_{B} \longrightarrow Pd@B-BO_{3}$	. x_/	$\mathbb{A}$
··· \_	_/ `	HO Visible Light	··· \=	. L
entry	Х	reaction condition variations	light	yield <sup><math>b</math></sup> (%)
1	Н	-	+	98
2	Н	-	-	13 <sup>c</sup>
3	Н	no K <sub>2</sub> CO <sub>3</sub>	+	-
4	Н	no Pd@B-BO <sub>3</sub>	+	-
5	Н	B-BO <sub>3</sub> as photocatalyst	+	trace
6	Н	Pd@C as photocatalyst	+	$16^d$
7	F	-	+	94
8	F	hole scavenger	+	21 <sup>e</sup>
9	F	radical scavenger	+	30
10	F	radical and hole scavengers	+	trace <sup>f</sup>

<sup>*a*</sup>Reaction conditions: iodobenzene (0.5 mmol), phenylboronic acid (0.55 mmol),  $K_2CO_3$  (0.75 mmol),  $Pd@B-BO_3$  (10 mg, 3 wt % Pd content), DMF/H<sub>2</sub>O (1.5 mL/1.5 mL), white LED lamp (1.2 W/ cm<sup>2</sup>), water bath, room temperature, 2 h. <sup>*b*</sup>Isolated yields after chromatography. <sup>*c*</sup>In dark, 5 h. <sup>*d*</sup>6 mg of Pd@C (5 wt % Pd content). <sup>*c*</sup>21% yield of 4-fluorobiphenyl and 17% yield of 4,4'-difluorobiphenyl. <sup>*f*</sup>Trace amount of 4-fluorobiphenyl and 8% yield of 4,4'-difluorobiphenyl.

trace conversion, and by extending the reaction time to 5 h, a conversion of 13% was observed (entry 2). This is similar to previous report on reactivity of Pd NPs at room temperature in dark.<sup>46</sup> No conversion was also observed without base (entry 3), which is essential to activate boronic acid and facilitate transmetalation.<sup>4</sup> Bare B-BO<sub>3</sub> without immobilization of Pd NPs as a control experiment only led to trace yield of the product, which is likely obtained due to the residual amount of Pd (~50 ppm) present in B-BO<sub>3</sub> after its preparation. Using Pd@C as photocatalyst led to a conversion of 16%, indicating a minor contribution of the Pd plasmonic effect compared to the photocatalytic activity afforded by the hybrid heterojunction between Pd and B-BO<sub>3</sub>.

To understand the specific role of the photogenerated electron-hole pairs during the photocatalytic Suzuki coupling reaction, a hole (diisopropylethylamine (DIPEA)) and a radical scavenger (benzoquinone) were added to the reaction mixture, respectively. In the same time, the occurrence of a possible homocoupling of both aryl reactants was also investigated. 4-Fluoroiodobenzene was taken as the model aryl halogenide in order to differentiate the homocoupled products. Under the same reaction condition as entry 1, 4-fluorobiphenyl; as product was obtained in a yield of 94% (entry 6). By adding DIPEA, i.e., when the hole was blocked, 4-fluorobiphenyl was obtained with a yield of 21%, as well as yielding the homocoupled side product 4,4'-difluorobiphenyl with a conversion of 17% (entry 8). Via addition of benzoquinone, where the generated electron was blocked, 4-fluorobiphenyl was still obtained in a yield of 30% without any observation of homocoupled side product (entry 9). By blocking both hole and electron upon addition of both scavengers, only traces of 4fluorobiphenyl were obtained, along with 8% of the homocoupled 4,4'-difluorobiphenyl (entry 10). It can be observed that both generated hole and electron pair were essential for the light-induced Suzuki coupling reaction. And by only blocking one of the photogenerated electron-hole pairs, Pd@B-BO3 was still active enough to precede the coupling reaction with one activated aryl species under lowered reaction rate.

On the basis of the observations during the screening and control experiments, we propose a possible reaction mechanism as displayed in Figure 2. Upon light irradiation, charge separations in the form of electron-hole pairs can be generated within the semiconductive polymer B-BO<sub>3</sub>. The photoexcited energetic electrons further amplify the Schottky effect by migrating toward the noble metal center (i.e., Pd NPs in this case). With the Pd NPs functioning as active center, the C–I bond of iodobenzene is attacked by the photogenerated



**Figure 2.** Suggested reaction mechanism of the photocatalytic Suzuki coupling via the light-induced heterojunction at the interface of B-BO<sub>3</sub> and Pd NPs.

electrons. Xiao et al. showed via the density functional theory (DFT) calculation, when an electron enters an unoccupied orbital of the iodobenzene molecule, the C–I bond elongates from 0.214 to 0.300 nm,<sup>35</sup> facilitating the cleavage of the C–I bond and yielding a transient radical anion, which initially forms an aryl complex with Pd. At the same time, the hole inside the semiconductive polymer B-BO<sub>3</sub> activates the C–B bond of phenylboronic acid, which is transferred into an electronically negative  $B(OH)_3^-$  species by catching an OH<sup>-</sup> from the basic reaction medium, forming another aryl Pd complex. The remaining steps, the reductive elimination and transmetalation, should not be affected by the photoactivation and are followed by the formation of the final product.<sup>47,48</sup>

We then further tested the feasibility of  $Pd@B-BO_3$  as photocatalysts for a series of Suzuki coupling reactions of phenylboronic acids with various aryl halides. As listed in Table 2, aryl iodides (for example entries 6 and 10), as expected, were

Table 2. Scope of the Photocatalytic Suzuki Coupling Reaction with Various Substituents Using  $Pd@B-BO_3$  as Photocatalyst<sup>a</sup>



<sup>*a*</sup>Reaction conditions: arylhalide (0.5 mmol), phenylboronic acid (0.55 mmol),  $K_2CO_3$  (0.75 mmol), Pd@B-BO<sub>3</sub> (10 mg, 3 wt % Pd content), DMF/H<sub>2</sub>O (1.5 mL/1.5 mL), white LED lamp (1.2 W/cm<sup>2</sup>), water bath, room temperature. <sup>*b*</sup>Isolated yields after chromatography.

converted more readily than their bromide counterparts (entries 14 and 15), which also showed good to excellent yields. Iodobenzene with electron-donating groups (CH<sub>3</sub>, OH, see entries 12 and 13) showed lower conversion rates when compared to those with electron-withdrawing groups such as F, Br, or NO<sub>2</sub>. *Ortho*-substituted substrates showed lower reactivity compared to other substituted positions on the substrates (entries 11 and 16), which could be caused by steric hindrance during the coupling reaction.

The coupling of iodobenzene and phenylboronic acid were carried out repeatedly under the same reaction condition as entry 1 in Table 1. Biphenyl was obtained without significant loss in yield, demonstrated the stability and reusability of Pd $BO_3$  as photocatalyst (Figure S11 in Supporting Information). TEM images of the used  $Pd@B-BO_3$  showed a similar structure as the unused one, while a slight weight loss of Pd was determined via ICP (Figure S9 in Supporting Information).

In conclusion, this work demonstrated that  $Pd(@B-BO_3)$ , a type of metal-immobilized microporous polymer semiconductor photocatalyst, can be used as efficient, heterogeneous photocatalysts for the Suzuki coupling reactions via the photoamplified Schottky effect at the metal—semiconductor interface. The coupling reactions of aryl halides with arylboronic acid yielded excellent conversions in best cases under visible light irradiation at room temperature. Given the heterogeneous nature, the photocatalyst could be easily separated and recycled for further coupling reactions without significant loss in activity. We also envision that this novel genre of photocatalysts could be applied to other classic crosscoupling reactions, such as Sonogashira, Stille, Hiyama, and other catalytic reactions.

## ASSOCIATED CONTENT

#### Supporting Information

Polymer synthesis, general procedure of the photocatalytic Suzuki coupling reaction, FT-IR, <sup>1</sup>H, <sup>13</sup>C, solid state <sup>13</sup>C CP/ MAS NMR and EPR spectra,  $N_2$  sorption isotherms, and pore size distribution. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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