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# Palladium–cadmium sulfide nanopowder at oil–water interface as an effective catalyst for Suzuki–Miyaura reactions

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S. Jafar Hoseini, Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj 7591874831, Iran. Email: jhosseini@yu.ac.ir; sjhoseini54@yahoo.com A simple and effective strategy is described for the synthesis of Pd–CdS nanopowder by the reduction of an organopalladium(II) complex,  $[PdCl_2(cod)]$  (cod = *cis,cis*-1,5-cyclooctadiene), in the presence of CdS quantum dots (QDs) at a toluene–water interface. We investigated the impact of addition of CdS QDs on catalytic activity of Pd nanoparticles (NPs). The Pd–CdS nanopowder functions as an efficient catalyst for Suzuki–Miyaura reactions for the formation of carbon–carbon bonds. There is a high electron density on Pd NPs and due to their high electron affinity they behave as an electron scavenger from CdS increasing the rate of oxidative addition, which is the rate-determining step of the catalytic cycle, and, just as we expect, the C–C coupling reaction with the Pd–CdS nanopowder is faster and occurs in less time than that with Pd nanocatalysts. Compared to classical reactions, this method consistently has the advantages of short reaction times, high yields in a green solvent, reusability of the catalyst without considerable loss of catalytic activity and low cost, and is a facile method for the preparation of the catalyst.

## KEYWORDS

oil-water interface, organopalladium complex, quantum dot, Suzuki-Miyaura reaction

# **1 | INTRODUCTION**

Palladium-catalysed Suzuki–Miyaura cross-coupling (SMC) reactions are a powerful tool for the formation of new carbon–carbon bonds and are routinely used in fine chemicals research and development and in pharmaceutical discovery laboratories.<sup>[1]</sup> Approaches for significantly improving heterogeneous Pd-based nanoparticle (NP) catalysts are still rare at the moment, as electron density within the metal could previously not be easily modified on that scale.<sup>[2]</sup> We are interested in enhancing the activity of heterogeneous Pd-based NP catalysts by increasing their electron density via support effects. Solar light absorption is a convenient and sustainable method for generating electronically excited states of photocatalysts.<sup>[3,2]</sup>

In recent years, colloidal II–VI semiconductor nanostructures,<sup>[4]</sup> often known as quantum dots (QDs), have been commonly investigated because of their special optical properties including broad absorption, excellent photostability and narrow emission, which in light-emitting diodes<sup>[5]</sup> enable their potential applications in solar cells,<sup>[6]</sup> biomedical labelling,<sup>[7]</sup> etc. Cadmium sulfide (CdS), in the form of semiconductor QDs, has a direct band gap (2.63 eV) and thus it becomes sensitive towards visible light. Among various modification strategies, coupling semiconductors with metal ions with a suitable work function has proven to be effective for enhancing the performance of catalysts. For example, Pd has a high work function value, which is very suitable for taking up electrons from the conduction band of CdS NPs.<sup>[8]</sup>

Herein, we demonstrate a novel, facile, simple and costeffective method for the synthesis of Pd–CdS nanopowder. Our synthetic method is advantageous in the following respects. (1) It is a simple and less expensive synthesis of Pd–CdS nanopowder, only a beaker and syringe being required to produce a high-quality nanopowder of Pd–CdS in a short time. To the best of our knowledge, there is no report concerning fabrication of metal loading on QDs at a liquid–liquid interface. (2) So far various methods have been employed for the synthesis of Pd–CdS.<sup>[8,9]</sup> Using the organometallic precursor in the present work, i.e. [PdCl<sub>2</sub>(cod)] (cod = *cis*,*cis*-1,5-cyclooctadiene), being able to decompose in the presence of NaBH<sub>4</sub> as a reducing agent, it appears as a valuable alternative for the synthesis of Pd–CdS nanopowder. In recent years, application of organometallic complexes has appeared as an important alternative route for the synthesis of nanomaterials.<sup>[10]</sup>

In the study reported here, we prepared Pd–CdS nanopowder via a facile method, utilizing CdS as the semiconductor to absorb visible light and Pd as the electron scavenger. The Pd–CdS nanopowder was characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) and UV–visible spectroscopies. The Pd–CdS nanopowder exhibited a high catalytic activity in the SMC reaction in water as solvent. This composite was shown to act as an efficient semi-heterogeneous catalyst for the SMC reaction in aqueous solution under aerobic conditions and could be efficiently reused whilst retaining its inherent catalytic activity.

## 2 | EXPERIMENTAL

All of the chemical compounds were purchased from Merck or Sigma-Aldrich. The [PdCl<sub>2</sub>(cod)] complex was synthesized using a reported procedure.<sup>[111]</sup> TEM images were obtained with a Philips CM-10 microscope operated at 100 kV. XRD patterns were obtained using a Bruker AXS (D8 Advance) instrument employing the reflection Bragg–Brentano geometry with Cu K $\alpha$  radiation. UV–visible studies were carried out using a PerkinElmer Lambda 25 spectrophotometer. FT-IR spectra were recorded using a JASCO FT/IR-680 Plus spectrometer. <sup>1</sup>H NMR spectra were obtained with a Bruker 400 MHz Ultra-shield spectrometer using CDCl<sub>3</sub> as the solvent. The loading amounts of Pd and Cd were determined using an inductively coupled plasma (ICP) analyser (Varian Vista-Pro).

### 2.1 | Preparation of CdS QDs

Firstly, an aqueous solution of mercaptosuccinic acid (MSA; 0.525 g, 5 ml) was added to CdCl<sub>2</sub> solution (0.01 M, 50 ml). The reaction mixture was bubbled with nitrogen gas for 30 min to remove oxygen. Secondly, under the protection of nitrogen gas, the reaction mixture was heated under reflux at 110 °C. After the pH was adjusted to 11 with NaOH (1.0 M), 5.5 ml of Na<sub>2</sub>S (0.1 M) was added to the solution and the reaction mixture was heated under reflux for 4 h. Finally, the reaction mixture was cooled to room temperature, and ethanol was added, precipitating a yellow product.

## 2.2 | Preparation of Pd–CdS Nanopowder at Toluene– Water Interface

 $[PdCl_2(cod)_2]$  complex (1 mM) in toluene (25 ml) was sonicated for 15 min to prepare a yellow-coloured solution. This solution was stood in contact with distilled water (25 ml) containing CdS QDs (1 mM) in a beaker (100 ml). Once the two layers were stabilized, 10 ml of aqueous NaBH<sub>4</sub> (0.1 M) was injected into the aqueous layer using a syringe with minimal disturbance to the toluene layer. The onset of reduction was marked by a coloration of the toluene–water interface. With the passage of time, the colour became more vivid, finally resulting in a film at the toluene–water interface. The organic and aqueous layers above and below the film were, however, transparent. The ICP analysis results for the amounts of Pd and Cd in the powder were 8.4 and 2.21%, respectively.

## 2.3 | General Procedure for SMC Reaction

In a typical reaction, 5.00 ml of water, 1.00 mmol of K<sub>2</sub>CO<sub>3</sub>, 0.50 mmol of aryl halide, 0.75 mmol of phenylboronic acid or 2-methylphenylboronic acid, and Pd-CdS nanopowder were mixed. Catalyst containing a certain amount of Pd (0.00004-0.012 mmol; for Pd-CdS nanopowder catalyst containing 8.4 wt% Pd, corresponding to 0.051-15.4 mg of catalyst) was added to the mixture. ICP analysis indicated that the ratio of Pd to Cd was 3.8:1. If the total amount of the catalyst used was less than 1.0 mg, a water dispersion of the catalyst with a concentration less than 1.0 mg ml<sup>-1</sup> was first prepared and then a small amount of the dispersion was taken and used as the catalyst. The mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the catalyst was separated from the reaction mixture by filtration, and then dichloromethane  $(3 \times 5 \text{ ml})$  was added to the reaction mixture. The organic phase was separated and dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent gave the pure desired product which was then characterized by comparing <sup>1</sup>H NMR and FT-IR spectra with those of authentic samples (details are given in the supporting information). The turnover number (TON; moles of product per mole of catalyst) and the turnover frequency (TOF; TON per time) were calculated on the basis of the amount of biaryl product formed. Also, a similar procedure was applied for the experiment in the dark.

## **3** | **RESULTS AND DISCUSSION**

#### 3.1 | Physicochemical Characterization of Catalyst

CdS QDs were prepared using a one-step route with MSA, CdCl<sub>2</sub> and Na<sub>2</sub>S as precursors in water. Here MSA and Na<sub>2</sub>S act as the capping agent and the sulfur source, respectively. A facile route for the synthesis of Pd–CdS nanopowder via a simple chemical reduction of  $[PdCl_2(cod)_2]$  complex at the oil–water interface with NaBH<sub>4</sub> at room temperature is demonstrated. The  $[PdCl_2(cod)_2]$  complex was selected as the Pd precursor due to its solubility in organic solvents and easy reduction to Pd(0) in the presence of reducing agents such as NaBH<sub>4</sub>.

The FTIR spectra of MSA and CdS QDs are shown in Figure 1. For MSA, absorption bands appear at 2643 and 2564 cm<sup>-1</sup>, which are attributed to CH<sub>2</sub>; a stronger absorption band appears at 1697 cm<sup>-1</sup>, which is assigned to C=O;



FIGURE 1 FT-IR spectra of (a) MSA and (b) CdS QDs

an absorption band appears at 1423 cm<sup>-1</sup>, which is assigned to C–O; and absorption bands of OH and SH appear around the 3200 cm<sup>-1</sup> (Figure 1a). The FT-IR spectrum of CdS QDs is shown in Figure 1(b). The characteristic peaks of the S–H and O–H stretching disappear, the peak of C=O shifts from 1697 to 1552 cm<sup>-1</sup> (145 cm<sup>-1</sup>) and the peak of C–O remains almost unchanged. The disappearance of the O–H peak and shifting of the C=O peak are due to deprotonation of the carboxyl group of MSA. As shown in Figure 2, the disappearance of the S–H peak is not due to the deprotonation of the sulfhydryl group of MSA which suggests that there must be a coordination interaction between Cd<sup>2+</sup> metal ion and MSA.

UV–visible spectra were used to analyse the optical properties of CdS and Pd–CdS nanopowder (Figure 3). The UV– visible spectrum (Figure 3a) shows the maximum absorption at *ca* 430 nm, revealing the CdS semiconductor QDs with



FIGURE 2 Schematic representation of formation of CdS QDs



FIGURE 3 UV-visible spectra of (a) CdS and (b) Pd-CdS nanopowder

band gap of 2.63 eV.<sup>[12]</sup> When the Pd NPs are introduced, a red shift is observed in the maximum absorption, likely because the presence of metallic Pd NPs contributes to enhanced absorption in the visible light region (Figure 3b).<sup>[12]</sup> As a result, the effective band gap of Pd–CdS decreases (2.06 eV). This distinct absorption in the visible light region suggests that the Pd–CdS nanopowder is more efficient at utilizing visible light, in the solar spectrum, a potential advantage to the photoelectrocatalytic efficiency for the catalytic SMC reaction.

The crystal structures of the compounds were investigated using XRD. Figure 4(a) shows the XRD pattern recorded for the CdS QDs. The four main diffraction peaks can be assigned as the (111), (220), (311) and (331) crystalline planes of CdS QDs.<sup>[13]</sup> Figure 4(b) shows the XRD pattern of the Pd–CdS nanopowder catalyst. The five main diffraction peaks can be assigned as the (111), (200), (220), (311) and (222) indices of face-centred cubic Pd(0),<sup>[14]</sup> and the diffraction peaks confirm the presence of CdS QDs (Figure 4b). Relative to the same reflections for Pd(0) and CdS QDs, the diffraction peaks of the Pd–CdS nanopowder are shifted, revealing decreased lattice parameters and a high level of alloying.

Recently, we have reported the formation of Pd(0) NPs from reduction of [PdCl<sub>2</sub>(cod)] complex at a toluene–water interface, the NPs having a mean diameter of approximately 4 nm.<sup>[14]</sup> Figure 5(a) and (b) shows TEM images of the Pd–CdS nanopowder, indicating spherical structures with mean diameter of approximately 5 nm that can obviously confirm Pd–CdS nanopowder formation.

## 3.2 | Catalytic Activity

To investigate the catalytic efficiency of Pd–CdS nanopowder, we began with SMC reaction of phenylboronic acid with bromobenzene as the model substrates (Table 1).  $K_2CO_3$  was used as the base to optimize the conditions of the reaction. The semi-heterogeneous catalyst was used in the present project. The Pd loading of the catalyst, which was obtained using ICP, was 4.2 µg in 0.051 mg of catalyst. The optimum amount of the catalyst is found to be 0.00004 mmol of Pd for Pd–CdS nanopowder catalyst, the



FIGURE 4 XRD patterns of (a) CdS QDs and (b) Pd–CdS nanopowder



**FIGURE 5** (a, b) TEM images Pd–CdS nanopowder and (c) histogram of particle size distribution

TABLE 1	Effects of solvent and temperature on SMC reaction of
bromobenz	ene with phenylboronic acid <sup>a</sup>

$H^{+} \qquad H^{B(OH)_{2}} \xrightarrow{Pd-CdS} \qquad H^{-CdS}$							
Entry	Solvent	Temp. (°C)	Yield (%) <sup>b</sup>				
1	H <sub>2</sub> O	r.t.	94				
2	EtOH	r.t.	70				
3	EtOH-H2O (1:1)	80	83				
4	H <sub>2</sub> O–CTAB	80	60				
5	H <sub>2</sub> O-SDS	80	40				
6	DMSO	r.t.	Trace				
7	THF	r.t.	Trace				

<sup>a</sup>Reaction conditions: 0.50 mmol of bromobenzene, 0.75 mmol of phenylboronic acid, 1.00 mmol of  $K_2CO_3$ , 5.0 ml of solvent, sunlight irradiation, the amount of supported Pd used is 0.00004 mmol, reaction time 1 h. <sup>b</sup>Isolated yield.

yield of biaryl being markedly is reduced when less catalyst is used. The reaction proceeds in the presence of Pd–CdS nanopowder in water and the desired product is obtained in 94% yield under mild conditions (room temperature)  $\{\#,32\}$  (Table 1, entry 1). Further, when the same reaction is carried out in a H<sub>2</sub>O–EtOH (1:1) solvent mixture at 80 °C, the desired product is obtained in 83% yield (Table 1, entry 3). Other solvents, such as ethanol, H<sub>2</sub>O–sodium dodecylsulfate (SDS), H<sub>2</sub>O–cetyltrimethylammonium bromide (CTAB), dimethylsulfoxide (DMSO) and tetrahydrofuran (THF), also afford low yields of the coupling product (Table 1, entries 2 and 4–7).

We investigated the impact of addition of CdS semiconductor ODs on the catalytic activity of the Pd NPs in the SMC reaction. For the coupling reaction of phenylboronic acid and bromobenzene, the reaction does not occur when using only pure CdS as catalyst. However, the Pd-CdS nanopowder catalyst shows excellent catalytic activity under the given conditions. The experimental results demonstrate the marked catalytic activity of Pd-CdS nanopowder with TON of 11 750 and TOF of 11 750 h<sup>-1</sup> (0.008 mol% Pd-CdS nanopowder, 94% yield at room temperature for 1 h) for SMC reaction of bromobenzene and phenylboronic acid. The catalytic activity of Pd-CdS nanopowder is much higher than that for the same SMC reaction catalysed by the Pd NP catalyst (0.8 mol% Pd NPs, 90% yield at 80 °C for 1.5 h, TON =112.5, TOF = 75  $h^{-1}$ ).<sup>[14]</sup> Also, for the same Pd loading (0.8 mol% Pd NPs), Pd NPs exhibit only 51% yield after 1 h. Thus, it may be concluded that Pd NPs deposited on the surface of CdS actually accelerate the rate of SMC reaction by stabilizing holes  $(h_{VB}^{+})$  in the valence band (VB) of CdS. As the work functions of Pd and CdS are 5.12 and 4.2 eV,<sup>[8]</sup> a built-in potential of 0.92 eV can form between Pd and CdS. The potential forces electrons to transfer from CdS to Pd NPs and results in electron-rich Pd NPs. Also, Pd is very much prone to electron capture<sup>[8]</sup> due to its high electron affinity, and thus can scavenge the photogenerated electrons from the CdS NPs. The electron-rich Pd NPs can activate bromobenzene and produce Pd-adsorbed aryl. Meanwhile, the photogenerated holes on the CdS surface can assist in activating phenylboronic acid molecules by cleaving the carbon-boron bond. Finally, the redox-activated species meet to couple to the final products. A schematic mechanism on the SMC reaction is illustrated in Figure 6.



FIGURE 6 Proposed mechanism for SMC reaction on Pd-CdS nanopowder catalyst

We then planned to evaluate the mechanism of the photocatalysis of Pd–CdS nanopowder in the SMC reaction. For this, we carried out the reaction of phenylboronic acid with bromobenzene in the presence of Pd–CdS nanopowder in water without irradiation (dark reaction). The irradiation of sunlight is necessary for reaction. These studies suggest the suppression of electron transfer from CdS to Pd NPs in the absence of sunlight. Furthermore, without irradiation of sunlight, only trace yield is observed which highlights the importance of irradiation to the catalytic activity of the system.

The SMC reaction of various aryl halides, even aryl chloride derivatives, was examined under optimal reaction conditions to show the high catalytic activity of the Pd–CdS nanohybrid. The results are summarized in Table 2. To avoid the homo-coupling product, we used different aromatic rings for halide and boronic acid (Table 2 entries 4–11).



For example, when Pd–CdS nanopowder was used as catalyst, the SMC reactions of deactivated aryl chloride including chlorobenzene, 1-chloro-4-nitrobenzene and



FIGURE 7 Recycling result for coupling reaction of bromobenzene with phenylboronic acid in the presence of Pd–CdS nanopowder

		$G' \rightarrow G' + C' +$	$\begin{array}{c} B(OH)_2 \\ \hline \\ K_2CO_3, H_2O, r.t., \\ \text{sunlight} \end{array}$	G R G		
		$\begin{split} \mathbf{Y} &= \mathbf{C},  \mathbf{N} \\ \mathbf{G} &= \mathbf{H},  \mathbf{Me},  \mathbf{NO}_2 \\ \mathbf{G}' &= \mathbf{H},  \mathbf{OMe} \\ \mathbf{X} &= \mathbf{CI},  \mathbf{Br},  \mathbf{I} \\ \mathbf{R} &= \mathbf{H},  \mathbf{Me} \end{split}$	a; $Y = C$ , $G' = H$ , $R = H$ 1a; $G = H$ , 2a; $G = Me$ , 3a; 1b; $Y = C$ , $G = H$ , $G' = OM$ 1c; $Y = N$ , $G = H$ , $G' = H$ , $F$ d; $Y = C$ , $G = H$ , $G' = H$ , $F$ 1e; $Y = C$ , $G = H$ , $G' = OM$	$G = NO_2, 4a; G = CN$ e, R = H R = H $= Me; 1d; G = H, 2d; G = NO_2$ e, R = Me		
Entry	Substrate	ArB(OH) <sub>2</sub>	Product	Time (h); yield $(\%)^a$	TON <sup>b</sup>	TOF $(h^{-1})^b$
1		B(OH) <sub>2</sub>		0.35, 96	12 000	34 286
2	Br	B(OH) <sub>2</sub>	$\langle \rangle - \langle \rangle$	1, 94	11 750	11 750
3	ci Ci	B(OH) <sub>2</sub>		2, 82	10 250	5 125
4	Br CH3	B(OH) <sub>2</sub>	CH3	1.5, 80	10 000	6 667
5		B(OH) <sub>2</sub>		1.33, 76	9 500	7 143
6	CI	B(OH) <sub>2</sub>		1.4, 79	9 875	7 054
7	CI OCH3	B(OH) <sub>2</sub>		2.5, 73	9 125	3 650
8	CIN	B(OH) <sub>2</sub>		9, 80	10 000	1 111
9	CI	B(OH) <sub>2</sub>		1.8, 82	10 250	5 694
10	CI OCH3	B(OH) <sub>2</sub>		2.37, 80	10 000	4 219
11		B(OH) <sub>2</sub>		1.28, 79	9 875	7 715

TABLE 2 SMC reaction of aryl halides with phenylboronic acid or 2-methylphenylboronic acid catalysed by Pd–CdS nanopowder under sunlight irradiation

#### <sup>a</sup>Isolated yield.

<sup>b</sup>See Section 1.3 for the calculation of TONs and TOFs.





FIGURE 8 TEM image of Pd–CdS nanopowder after seven catalytic cycles

2-chloropyridine proceed with high yields of 82, 76 and 80%, respectively (Table 2, entries 3, 5 and 8). The SMC reactions of activated aryl chlorides with different substituents also give good yields (Table 2, entries 6, 7 and 9–11). The results unambiguously indicate that aryl iodides and aryl bromides are involved in the fast steps of the catalytic cycle of the SMC reaction (Table 2, entries 1, 2 and 4). Sterically hindered aryl chlorides and arylboronic acids are effective as substrates (Table 2, entries 7 and 10). Generally, the catalytic cycle of the SMC reaction includes three steps: (1) oxidative addition, (2) transmetalation, and (3) reductive elimination.<sup>[14]</sup> Normally, the activity of aryl halides decreases in the order of I > Br > Cl and electron-deficient aryl halides are usually more active than electron-rich ones. Thus, the oxidative addition step is generally considered as the rate-determining step. In the oxidative addition step, Pd(0)acts as a nucleophile and preferentially attacks the most electron-deficient position. It should be noted that the Pd-CdS nanopowder behaves as a very good catalyst in the SMC reaction. The Pd-CdS nanopowder catalyst, compared to Pd NP catalyst due to the presence of CdS groups, exhibits

Solvent Entry G Catalyst Base Temp. (°C) Time (h) Yield (%) Ref. 1 Н  $Pd(OAc)_2.(1f)_2^a$ H<sub>2</sub>O-EtOH (3:2) K<sub>2</sub>CO<sub>3</sub> 80 48 33 [16] 2 Η  $Pd(OAc)_2.(1 g)_2^b$ H<sub>2</sub>O-EtOH (3:2) K<sub>2</sub>CO<sub>3</sub> 80 10 73 [16] 3 Н  $Pd(OAc)_2^c$ H<sub>2</sub>O Na<sub>2</sub>CO<sub>3</sub> 150-170 5 min 45 [17] 4 Н  $NAP-Mg-Pd(0)^d$ DMA 130 2-6 65 K<sub>3</sub>PO<sub>4</sub> [18] H<sub>2</sub>O-DMF (1:1) 5 Н Pd(II)-MWCNTs<sup>e</sup> K<sub>2</sub>CO<sub>3</sub> 65 7 53 [19] Pd FS<sup>f</sup> Н 4 75 6  $H_2O$ K<sub>2</sub>CO<sub>3</sub> 80 [14] 7 Н Pd/RGO<sup>g</sup>  $H_2O$ K<sub>2</sub>CO<sub>3</sub> 80 3 80 [14] 8 Η  $PdZn^{h}$ EtOH-H<sub>2</sub>O (1:1) 80 8 70 [14] K<sub>2</sub>CO<sub>3</sub> 9 Н PdPtZn<sup>i</sup> H<sub>2</sub>O-CTAB 80 2 80 [14] K<sub>2</sub>CO<sub>3</sub> 10 Н Pd/Fe<sub>3</sub>O<sub>4</sub>/RGO<sup>j</sup>  $H_2O$ K<sub>2</sub>CO<sub>3</sub> 80 2.5 85 [14] 11 Η Pd-dS K<sub>2</sub>CO<sub>3</sub> 2 82 This work H<sub>2</sub>O r.t. 12  $NO_2$  $Pd(OAc)_2.(1f)_2^a$ H<sub>2</sub>O-EtOH (3:2) K<sub>2</sub>CO<sub>3</sub> 10 67 [16] r.t. Na<sub>2</sub>[PdCl<sub>4</sub>]<sup>k</sup> 13  $NO_2$ H<sub>2</sub>O-DMSO KF, K<sub>3</sub>PO<sub>4</sub> 80 18 90 [20] 14  $NO_2$ NAP-Mg-Pd(0)<sup>d</sup> DMA K<sub>3</sub>PO<sub>4</sub> 130 2-6 90 [18] Pd/Fe<sub>3</sub>O<sub>4</sub>/RGO<sup>j</sup> 15  $NO_2$ H<sub>2</sub>O K<sub>2</sub>CO<sub>3</sub> 80 1.5 78 [14] 16  $NO_2$ Pd FS<sup>f</sup>  $H_2O$ K<sub>2</sub>CO<sub>3</sub> 80 2.5 70 [14] 17 Pd/RGO<sup>g</sup> NO<sub>2</sub> H<sub>2</sub>O K<sub>2</sub>CO<sub>3</sub> 80 1.5 74 [14] 18  $NO_2$ Pd-CdS  $H_2O$ K<sub>2</sub>CO<sub>3</sub> r.t. 1.33 76 This work

TABLE 3 Catalytic performance of various Pd-based catalysts in the coupling of chlorobenzene and 1-chloro-4-nitrobenzene with phenylboronic acid

<sup>a</sup>Pd(OAc)<sub>2</sub>.(1f)<sub>2</sub> (2 mol%) (1f = 1,1,3,3-tetramethyl-2-*n*-butylguanidine).

<sup>b</sup>Pd(OAc)<sub>2</sub>.(1 g)<sub>2</sub> (2 mol%) (1 g = 1,1,3,3-tetramethyl-2-sec-butylguanidine); TBAB (0.1 equiv.) as additive.

ePd-Schiff base@MWCNTs (0.2 mol%).

<sup>f</sup>Pd FS NP (0.8 mol%).

<sup>g</sup>Pd/RGO NP (0.48 mol%).

<sup>h</sup>PdZn NP (1.5 mol%).

<sup>i</sup>PdPtZn NP (1 mol%).

<sup>j</sup>Pd/Fe<sub>3</sub>O<sub>4</sub>/RGO nanohybrid (0.36 mol%).

<sup>k</sup>Na<sub>2</sub>[PdCl<sub>4</sub>] (0.5 mol%).

<sup>&</sup>lt;sup>c</sup>Pd(OAc)<sub>2</sub> (0.4 mol%).

<sup>&</sup>lt;sup>d</sup>NAP-Mg-Pd(0) (3 mol%).

a faster oxidative addition. As mentioned, in the Pd–CdS nanopowder donation of electrons from CdS to Pd NPs improves the reactivity of the catalyst compared to Pd NPs.

Good recyclability is the main advantage of heterogeneous or semi-heterogeneous catalysts. From an industrial point of view, the reusability of a catalyst is important for large-scale operation. To test the recyclability of the Pd–CdS nanopowder catalyst in the C–C coupling of bromobenzene and phenylboronic acid, the catalyst was reused for seven times after filtering and drying, without noticeably losing activity (Figure 7). The recovered catalyst was dried and observed using TEM analysis. The particles of the Pd–CdS nanopowder remain the same size, and no considerable aggregation phenomenon is observed after seven cycles from TEM imaging (Figure 8). Also, the used catalyst was analysed using ICP and no discernible leaching of Pd is observed.

TON and TOF, which are measures of the efficiency of a catalyst, totally depend on the Pd concentration. Guo and co-workers reported that the SMC reaction over a Mott–Schottky-type Pd/SiC catalyst gave a TOF of 1053  $h^{-1}$ .<sup>[3]</sup> Fox and co-workers reported that the SMC reaction over a Pd NP cored G-3 dendrimer catalyst gave a TOF of 2175  $h^{-1}$ .<sup>[15]</sup> In the current study using Pd–CdS nanopowder as a catalyst, a higher TOF of 34 286  $h^{-1}$  is observed for the SMC reaction of iodobenzene with phenylboronic acid.

We compared our results with those for Pd-based catalysts reported in the past few years for the SMC reaction, taking the reactions of chlorobenzene and 1-chloro-4-nitrobenzene with phenylboronic acid as two examples (Table 3).<sup>[16–20]</sup> Though some of these catalysts can also lead to high yields, the following factors make our catalyst superior to the others for these reactions: (i) excellent recyclability without loss of catalytic activity in water solvent at room temperature, (ii) the catalyst is prepared by a facile, efficient and low-cost method, (iii) excellent results are obtained in short reaction times using low catalyst loading and (iv) large TON indicates that the catalyst is stable and very long-lived.

## 4 | CONCLUSIONS

The study presented shows that Pd–CdS nanopowder catalyst can harvest natural sunlight and catalyse the SMC reaction. The catalytic activity of Pd NPs under irradiation can be evidently increased using the photoactive CdS semiconductor QDs. This can be attributed to the transfer of photogenerated electrons in CdS to Pd NPs. The obtained Pd–CdS nanopowder catalyst could be dispersed homogeneously in water by sonication for 10 min; the catalyst was injected into the flask using a syringe and further used as an excellent semi-heterogeneous catalyst for the SMC reaction. According to the three following points, we have demonstrated a semiheterogeneous process: (i) the catalyst is insoluble in the

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micelle medium, (ii) the catalyst leaching was calculated from ICP analysis and no discernible leaching of Pd was observed (this is the most important point) and (iii) catalyst recovery is done by solvent decantation. The catalyst can be handled easily as it is very stable in air and can be easily removed from the reaction mixture by filtration. By employing this novel heterogeneous photocatalyst, the SMC reaction can proceed at room temperature under the irradiation of natural sunlight. The present work will inspire the further exploitation of semiconductor-supported metal NPs as photocatalysts for a wide range of organic transformations driven by visible light, even natural sunlight.

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