

Photothermal Suzuki Coupling Over a Metal Halide Perovskite/Pd Nanocube Composite Catalyst

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Abstract

The development of improved catalysts capable of performing the Suzuki coupling reaction has attracted considerable attention. Recent findings have shown that the use of photoactive catalysts improves the performance, while the reaction mechanism and temperature-dependence performance of such systems are still under debate. Herein, we report Pd nanocubes/CsPbBr₃ as an efficient catalyst for the photothermal Suzuki reaction. The photo-induced and thermal contribution to the overall catalytic performance has been investigated. At temperatures around and below 30 °C light controls the activity, while thermal catalysis determines the reactivity at higher temperature. The Pd/CsPbBr₃ catalyst exhibits 11 times higher activity than pure CsPbBr₃ at 30 °C due to reduced activation barrier and facilitated charge carrier dynamics. Furthermore, the alkoxide radicals (R-O[•]) for Suzuki reaction are experimentally and theoretically confirmed, and photogenerated holes are proven to be crucial for cleaving C-B bonds of phenylboronic acids to drive the reaction. This work prescribes a general strategy to study photothermal catalysis and offers a mechanistic guideline for photothermal Suzuki reactions.

Keywords: Photothermal catalysis; Metal halide perovskites; Pd nanocube; Suzuki coupling reaction; Temperature-dependent performance

1. Introduction

The Suzuki coupling reaction is one of the most important organic synthetic methods for C-C bond formation.^{1,2} While the reactions were initially performed using Pd complexes as homogeneous catalyst, a lot of research has been focused on the fabrication of solid catalysts using Pd nanoparticles (NPs).³⁻⁵ Pd is the preferred catalyst for thermally driven Suzuki coupling reactions and temperature significantly influences the performance. The catalytic activity of Pd NPs is reported to be associated with the particle morphology, i.e., exposing different facets; cubic Pd has been found to present an improved reactivity due to the presence of the (100) crystal facets.⁶ Recent research has shown the possibility to enhance the Suzuki coupling reaction under light irradiation through the use of photocatalytic supports, such as TiO₂, C₃N₄, SiC, WS₂, in combination with Pd NPs.^{3,5,7} Yet, the temperature-dependent photocatalytic activity of Pd-photocatalytic support hybrids is seldomly investigated. Bai et al. reported photocatalytic Suzuki coupling reactions with Pd and TiO₂ decorated carbon nanofibers, and they showed that the performance increased from 30 to 50 °C.⁸ However, the precise contribution of photo- and thermal catalysis at different temperatures has not been clarified since the photoactivity of TiO₂ also improves with the increased temperature.⁹ Recently, metal halide perovskites (MHPs) have emerged as promising photocatalysts exploiting their excellent opto-electronic properties such as tunable bandgap, strong light absorption coefficient, long carrier diffusion length, small exciton binding energy, and low-cost solution-processing.¹⁰ Although MHPs-based photocatalysts have been explored for various chemical processes, their performance in driving Suzuki coupling reactions has not yet been explored.

On the other hand, the underlying reaction mechanisms of photocatalytic Suzuki couplings are still under debate. For instance, the exact role of photogenerated holes is

controversial. Antonietti et al. proposed that the photoexcited holes can assist in cleaving C-B bond in phenylboronic acids,⁴ while Kim and coworkers claimed that the holes will be trapped by the solvent but not participate in the coupling reaction.⁵ Moreover, the reaction intermediates generated from the phenylboronic acids remain uncertain. Specifically, both OH⁻ and CO₃²⁻ anions have been reported to activate phenylboronic acids to form intermediates.^{3, 4} Additionally, the alkoxide ion (EtO⁻) is also speculated to activate the phenylboronic acids,¹¹ while direct experimental evidence is lacking. Summarizing, there is no consensus on the photocatalytic Suzuki reaction mechanism.

Herein, we report Pd nanocubes (NCs) deposited on the photoactive CsPbBr₃ MHP as efficient photothermal Suzuki coupling catalyst using solar irradiation (AM 1.5G) at near ambient temperature conditions. The precise contribution of the photo-induced and thermal catalysis to the overall performance is resolved. At mild conditions, below 30 °C, the photocatalytic reaction is responsible for the majority of the conversions, while thermally driven catalysis determines the reactivity at higher temperature. Benefiting from the synergistic photothermal effect leading to a reduced activation barrier, the Pd/CsPbBr₃ catalyst exhibits 11 times higher activity than pure CsPbBr₃ and 4 times for Pd. Through advanced characterization it is shown that the CsPbBr₃ metal halide perovskite (MHP) efficiently collects the solar irradiation and the presence of Pd NPs mediates in the efficient charge extraction through Schottky barrier formation and surface defect passivation. Further, through a set of control experiments and theoretical calculations, the reaction radicals, *i.e.*, alkoxides (R-O⁻), are confirmed and the photogenerated holes are revealed to be crucial for the cleavage of the C-B bonds of phenylboronic acids to boost the Suzuki coupling reaction.

2. Results and discussion

To prepare the CsPbBr₃ and Pd/CsPbBr₃ hybrid catalysts, a room-temperature antisolvent precipitation method was adopted,¹² in which the Pd NCs were synthesized based on reported methods.¹³ X-ray diffraction (XRD) patterns (Figure S1) reveal that the pure CsPbBr₃ possesses an orthorhombic (Pnma) phase and the pure Pd has a cube morphology.^{13, 14} Due to the low Pd loading no typical diffraction peaks assigned to Pd are detected in the hybrids.¹³ Raman spectroscopy further confirms that CsPbBr₃ is the predominant material in the hybrids and Pd has no influence on the CsPbBr₃ structure (Figure S2). Scanning electron micrographs (Figure S3) show that the CsPbBr₃ and 3 wt% Pd/CsPbBr₃ composites have similar surface morphologies. Energy-dispersive X-ray spectroscopy proves the presence of Pd, Cs, Pb and Br elements in the samples (Figure S3e). Transmission electron microscopy (TEM) (Figure S4) shows the successful deposition of Pd NCs on the surface of CsPbBr₃ in which the average size of Pd is around 17.2 ± 0.7 nm. From high-resolution TEM images, the lattice spacings of CsPbBr₃ ((110)=0.42 nm) and Pd ((200)=0.20 nm) were identified.^{13, 15} Nitrogen physisorption data (Figure S5) shows that the surface area of CsPbBr₃ is similar with that of Pd/CsPbBr₃ (Table S1), suggesting the Pd deposition has a negligible effect on the materials surface. Through inductively coupled plasma-mass spectrometry (ICP-MS) the precise amount of Pd was determined to be 2.72 wt% in 3 the wt% Pd/CsPbBr₃ composite.

Next, the photocatalytic Suzuki coupling reaction of iodobenzene with phenylboronic acid as a model reaction was performed. Without catalyst, no Suzuki coupling product was detected (Figure 1a), and the pure CsPbBr₃ shows a 11% conversion and moderate selectivity (81%) with benzene as the main side product (Figure S6) after 4 h under 1-sun solar light irradiation at 30 °C. Notably, the catalytic

activity shows an impressive enhancement in the presence of Pd. The optimal 3 wt% Pd/CsPbBr₃ catalyst exhibits the highest conversion (96.5 %) with nearly 100% selectivity, an 11-fold improvement compared to pure CsPbBr₃. Further increasing Pd loading beyond 3% resulted in a reduced conversion, which could be attributed to competitive light absorption and enhanced charge recombination caused by Pd.¹⁶ Table S2 compares the catalytic performance of 3 wt% Pd/CsPbBr₃ catalyst from this work to other reported photocatalytic Suzuki coupling catalysts. The reaction protocol was further extended to the coupling of different aryl halides and phenylboronic acids (Table 1). All aryl iodides were converted into the corresponding products in high yields (entries 1-4), while the compound with electron-withdrawing substitutions (entries 1-3) show higher activity than that with electron-donating substitutions (entry 4). This can be explained by the fact that electron-withdrawing substituents result in an electron-deficient aromatic ring which facilitates the nucleophilic attack *via* the photogenerated electrons on the electron-rich Pd NPs.⁷ Besides, no steric hindrance effect was observed (entries 2 and 3). Also, phenylboronic acids with electron-donating or electron-withdrawing substituents can easily convert into their desired products (entries 5-8), without an obvious steric hindrance effect (entries 7 and 8). Moreover, the applicability of the Pd/CsPbBr₃ catalyst for bromobenzene derivatives and aryl chlorides was also investigated (entries 9-14), and excellent performance was achieved. The results of photocatalytic coupling with different aryl halides and phenylboronic acids suggest the versatility of 3 wt% Pd/CsPbBr₃ hybrid catalyst.

The effect of the light intensity on catalytic activity was investigated (Figure 1b). The purely thermal conversion was measured in the dark and the photo-induced contribution was obtained by subtracting this thermal activity from the overall photothermal conversion.³ This shows that there is an almost linear relation between

the photo-induced activity and the light intensity, indicating that light irradiation plays a key role in driving the Suzuki reaction in this system.^{3, 4}

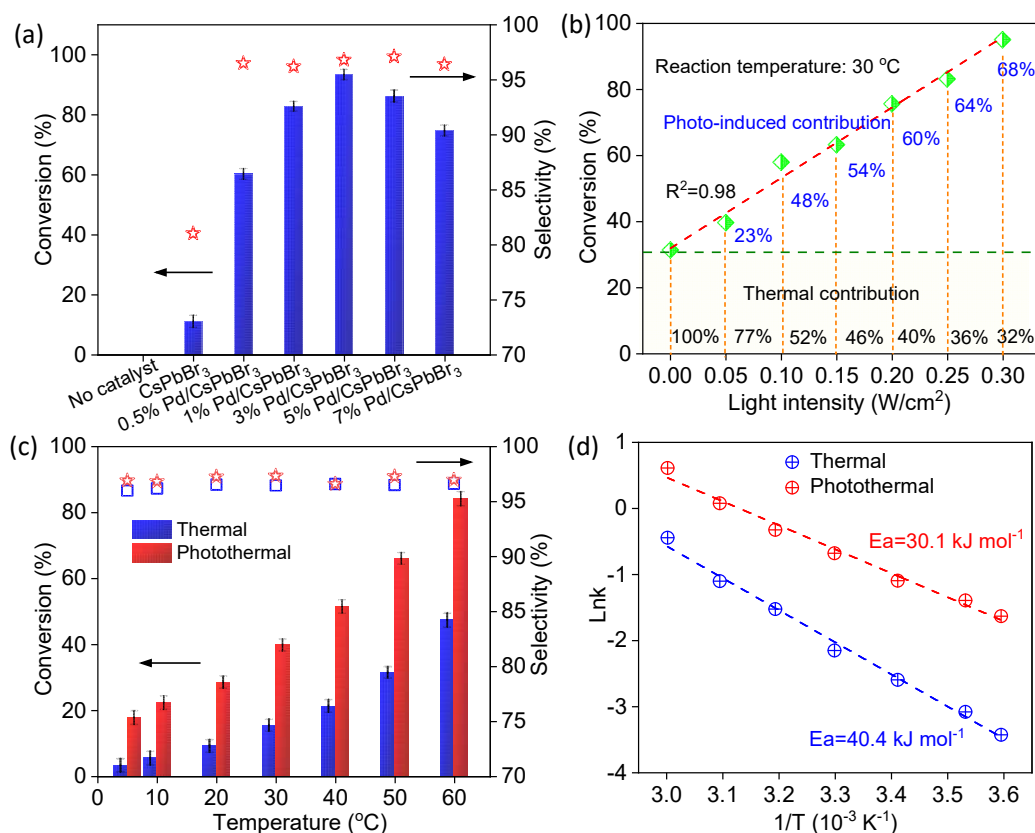
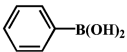
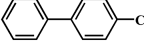
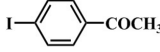
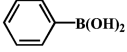
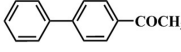
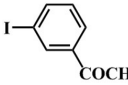
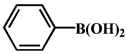
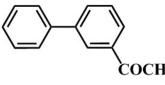
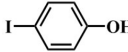
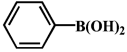
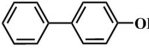
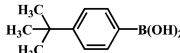
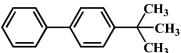
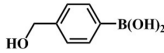
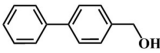
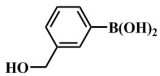
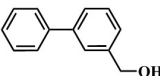
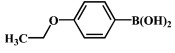
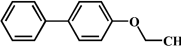
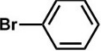
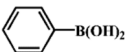
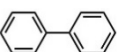
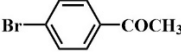
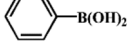
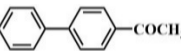
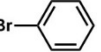
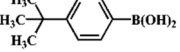
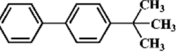
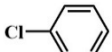
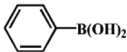
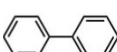
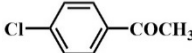
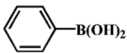
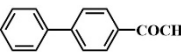
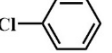
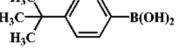
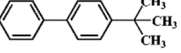


Figure 1. (a) The photocatalytic performance of Suzuki coupling reaction over CsPbBr₃ and Pd/CsPbBr₃ hybrids at 30 °C for 4 h under 1-sun irradiation. (b) The dependence of the catalytic activity of 3 wt% Pd/CsPbBr₃ on the solar light intensity at 30 °C for 4 h. (c) Thermal and photothermal Suzuki reactions under different temperatures (5-60 °C) for 1 h with 1-sun light irradiation. (d) Apparent activation energy derived *via* Arrhenius equation, where *k* represents the rate constant. Reaction conditions: 0.1 mmol iodobenzene, 0.12 mmol phenylboronic acid, 15 mg catalyst, 0.4 mmol Cs₂CO₃, 3 mL ethanol, simulated solar light (150 W Xe lamp, AM 1.5G), reaction time (4 h for a-b and 1 h for c).

Table 1. The catalytic performances of 3 wt% Pd/CsPbBr₃ catalyst for Suzuki reaction with different aryl halides and phenylboronic acids.^[a]

Entry	Reactant 1	Reactant 2	Main product	Conversion (%)	Selectivity (%)
1				99.6	99.5
2				99.2	99.6
3				99.5	99.4
4				90.8	98.7
5				96.5	99.2
6				93.7	99.3
7				92.6	99.6
8				92.0	99.1
9				88.3	99.3
10				86.7	99.0
11				87.0	98.9
12 ^b				65.8	98.3
13 ^b				64.3	99.1
14 ^b				65.1	98.6

^[a]Reaction conditions: 0.1 mmol aryl halides, 0.12 mmol phenylboronic acids, 15 mg catalyst, 0.4 mmol Cs₂CO₃, 3 mL ethanol, simulated solar light (150 W Xe lamp, AM

1.5G), reaction time (4 h, 30 °C). ^[b]Reaction conditions: 0.05 mmol aryl chlorides, 0.06 mmol phenylboronic acids, 20 mg catalyst, 0.2 mmol Cs₂CO₃, 3 mL ethanol, simulated solar light (150 W Xe lamp, AM 1.5G), reaction time (6 h, 30 °C).

To evaluate the contribution of thermal and photo-induced effect on the overall catalytic performance of the Pd/CsPbBr₃ composites, the Suzuki reaction was performed at controlled temperatures between 5 and 60 °C, while keeping the light irradiation constant at 1-sun. As shown in Figure 1c, with the increase of temperature, the catalytic performance of 3 wt% Pd/CsPbBr₃ increases gradually. Notably, below 30 °C, the photo-induced activity exceeds the thermal contribution of Pd. When using the pure constituents, for CsPbBr₃ only photo-induced activity was observed, while for Pd only thermal activity was measured. Additionally, it is worth noting that the activity of 3 wt% Pd/CsPbBr₃ is about double that of the sum of the conversions obtained by pure CsPbBr₃ and Pd (Figure S7), indicating the synergetic effect of photo and thermal.^{17, 18} By increasing reaction temperature to 60 °C, the contribution of photo-induced activity in total conversion clearly decreases. This may be attributed to the fact that thermally most of the reaction sites in Pd for Suzuki reaction are already activated and thus the effect of light on the performance is reduced accordingly.

Using the temperature dependent activity data, the apparent activation energy, derived *via* the Arrhenius equation (see Supporting Information and Figure S8),¹⁸ was calculated to be 40.4 and 30.1 kJ mol⁻¹ (Figure 1d) for thermal and photothermal catalysis, respectively. To explain this favourable contribution of the photogenerated charge carriers on the Suzuki reaction, theoretical calculations indicate that the photogenerated electron can weaken the C-I in iodobenzene thus simplifying the cleavage.¹⁹ The stability tests (Figure S9a) show no significant loss in activity even

after six reaction cycles with a total of 24 hours. XRD patterns do not show changes in crystal structure of the catalyst after recycling (Figure S9b), while ICP-MS tests show no Pd has leached during the reaction processes, and without changes in activity after catalytic separation (Figure S10). *In situ* temperature dependent XRD and Raman tests (Figures S11 and S12) confirm that the stability of the material under the applied reaction conditions. Both optical (absorbance and PL) characterization and XPS show that there is no observable halide exchange during the catalytic reaction process at higher temperature (60 °C) (Figure S13).

To understand the origin of the activity enhancement in Pd/CsPbBr₃ hybrids, the photophysical properties of these materials were studied. X-ray photoelectron spectroscopy (XPS) was first performed to investigate/determine the chemical structure and valence state of the materials. Figure S14a shows the two typical Cs 3d peaks located at 724.1 and 738.2 eV, which are assigned Cs 3d_{5/2} and Cs 3d_{3/2}, respectively.²⁰ After loading the Pd NCs, these peaks shift 0.15 eV toward higher binding energy, indicating that electrons transfer from CsPbBr₃ to Pd due to the formation of a Schottky junction.²¹ As a result, the presence of Pd can mediate in the efficient charge extraction in CsPbBr₃ (vide infra). A similar shift is also found in Pb 4f and Br 3d (Figures S14b and c). Additionally, the Pd 3d peaks with binding energies of 334.6 and 339.9 eV in 3wt% Pd/CsPbBr₃ (Figure S14d) correspond to Pd 3d_{5/2} and Pd 3d_{3/2}, respectively, showing a lower binding energy as compared to metallic Pd originating from electron enrichment on the Pd NCs.³

Photoelectrochemical characterizations were used to confirm the beneficial effect of Pd in charge transfer and separation in CsPbBr₃ materials. Transient on-off photocurrent measurements (Figure 2a) show that the 3 wt% Pd/CsPbBr₃ composite displays a higher photocurrent than pure CsPbBr₃. A similar trend is found in the

photocurrent response versus monochromatic light test, where an elevated current density for the Pd/CsPbBr₃ composite is observed (Figure 2b), indicating that the Pd incorporation can effectively promote the transfer and migration of photogenerated charge carriers.²² Moreover, the photocurrent density of 3 wt% Pd/CsPbBr₃ sample derived from cathodic polarization curves (Figure S15) also presents an obvious enhancement compared to pure CsPbBr₃ at the same potential range, agreeing well with bespoke observations.¹³ To under this enhancement in photocurrent, electrochemical impedance spectroscopy (EIS) was carried out to examine the charge transfer properties of the samples.²² The charge-transfer resistance for 3 wt% Pd/CsPbBr₃ (227 Ω) is much lower than that of CsPbBr₃ (353 Ω) (Figure 2c), indicating better efficiency in charge transfer within the Pd/CsPbBr₃, which is in agreement with its improved photocurrent.²³ Furthermore, the surface charge transfer efficiency (η_t) was calculated to be 36.5 % for CsPbBr₃ (Figure 2d); while in the presence of Pd, the η_t of Pd/CsPbBr₃ composite as high as 58.4 %, 1.6-fold higher than that of pure CsPbBr₃ (Figure S16), further confirming the faster transfer efficiency of photogenerated charge carriers.²⁴ Based on the above analyses, a schematic view representing the charge dynamics is depicted (Figure S17). Under light irradiation, the photogenerated electrons in CsPbBr₃ transfer to Pd, and the as-formed Schottky barrier at the interface will block the back-flow of electrons from Pd to CsPbBr₃, leading to efficient separation of photogenerated charge carriers.^{3, 4}

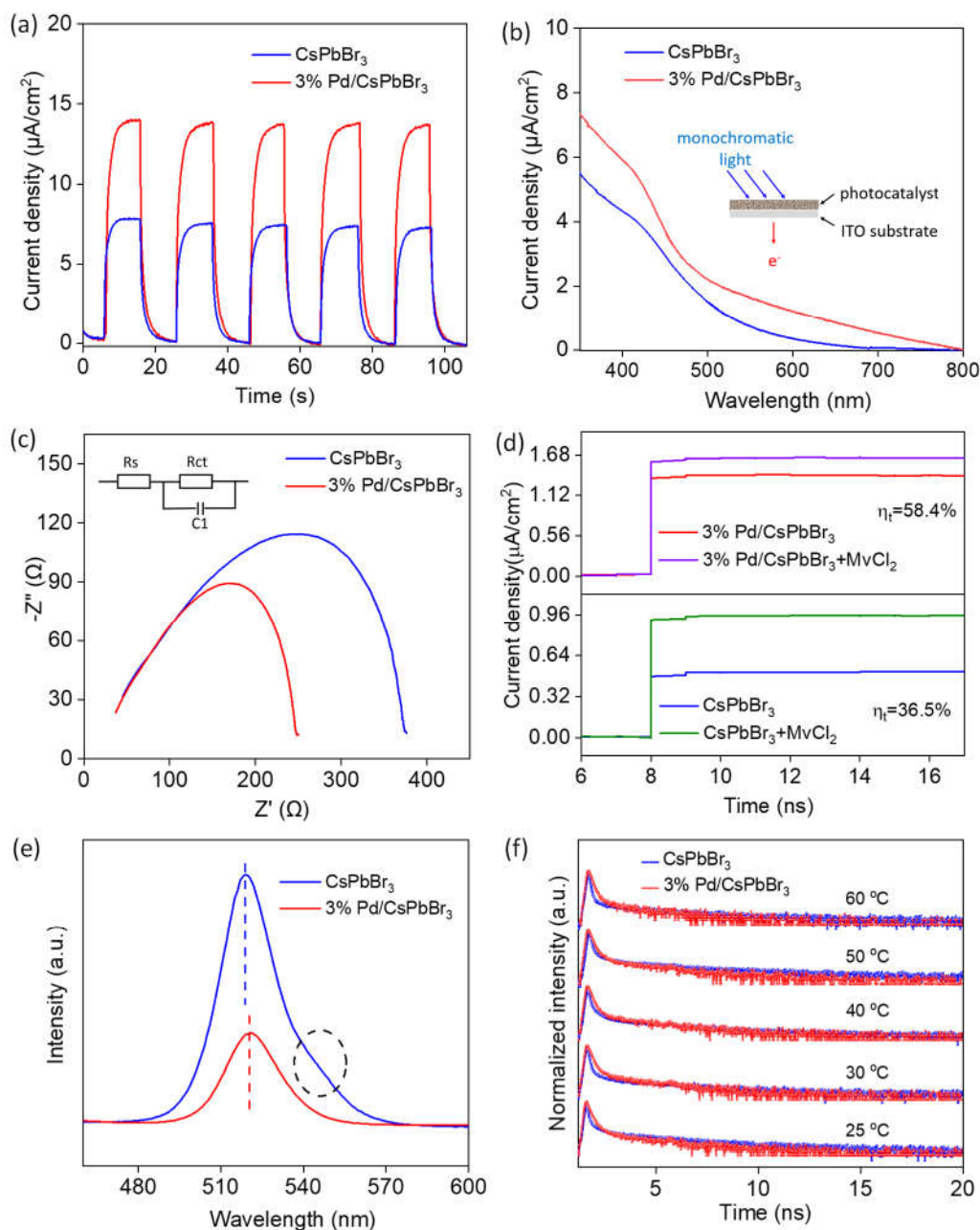


Figure 2. (a) Transient photocurrent, (b) Photocurrent response versus monochromatic light, (c) EIS Nyquist plots, (d) Surface charge transfer efficiency (η_t), (e) Steady-state PL spectra and (f) *In situ* temperature-dependent transient PL spectra of CsPbBr₃ and 3wt % Pd/CsPbBr₃ materials.

The optical absorption properties of the samples were characterized through UV-Vis diffuse reflection spectroscopy (DRS). The absorption spectrum of CsPbBr₃

(Figure S18a) reveals an absorption band edge at 551 nm, with a bandgap of 2.25 eV (Figure S18b).²⁵ No changes in bandgap after loading the Pd are observed, while the samples exhibit an enhanced absorption intensity at longer wavelengths, with color changing from orange-yellow to dark black (Figure S19). This can be ascribed to the light scattering of Pd and thus promoting the light absorption of CsPbBr₃ therefore contributing to catalytic activity enhancement.¹³

The photophysical processes in the CsPbBr₃ and Pd/CsPbBr₃ materials were examined through steady-state photoluminescence (PL) spectroscopy. The PL spectrum of CsPbBr₃ (Figure 2e) shows an emission peak at around 525 nm,²⁶ with a small shoulder located at ~550 nm which can be attributed to either surface defect or self-absorption.^{27, 28} A lower PL intensity in Pd/CsPbBr₃ hybrids was observed compared to CsPbBr₃ due to the suppressed radiative recombination.²¹ The small shoulder in the PL spectrum disappeared after the incorporation of Pd (Figures 2e and S20), which can be attributed to the surface passivation by Pd and thus reducing an unwanted recombination pathway for the photogenerated charge carriers.^{29, 30} Additionally, a red shift of the PL peak of the 3 wt% Pd/CsPbBr₃ sample is observed, which is further investigated by temperature-dependent (4.2-300 K) steady-state PL (Figure S21). Note that the PL peak of CsPbBr₃ maxima exhibit a blue-shift with increasing temperature (Figure S21c), originating from the temperature induced lattice expansion and its competition with the electron-phonon coupling.³¹ The electron-phonon coupling constants of these two systems, extracted from the temperature-dependence of the emission line width,³² are similar (Figure S21d), indicating no fundamental changes in the electron-phonon interactions in these two samples. Additionally, low temperature (77 K) absorption measurements show that both CsPbBr₃ and the Pd/CsPbBr₃ composite have similar absorption band edges (Figure

S22), further confirming that the Pd does not affect the intrinsic properties of CsPbBr₃.

To better understand the charge dynamics behind the temperature dependent activity behaviour, *in situ* temperature-dependent transient PL was performed (Figure 2f). The PL decays of the samples are analyzed using a sum of two exponential decays, where the extracted two decay constants τ_1 and τ_2 are associated with the bound exciton and free exciton recombination, respectively.³³ The lifetime of the 3 wt% Pd/CsPbBr₃ slightly increases as a function of temperature from 25 to 60 °C as compared to CsPbBr₃ (Figure S23), which can be attributed to the CsPbBr₃ surface defect passivation by Pd.¹⁹ To sum up, the above analyses revealed that the nature of the enhanced catalytic performance in Pd/CsPbBr₃ hybrids originating from the improved photo-electric properties. Moreover, the Pd nanoparticles in the catalyst composites not only serve as an electron reservoir enhancing the photogenerated charge separation in CsPbBr₃ (Figures 2 and S16) but also as source of catalytic sites for Suzuki couplings (Figure 1c and S7).

Next, the Suzuki coupling reaction mechanism was then systematically investigated. For the initiation of Suzuki reactions, anions like OH⁻ and CO₃²⁻ are generally reported to activate the phenylboronic acid to form C₆H₅-B(OH)₃⁻ and C₆H₅-B(OH)₂CO₃²⁻ intermediates to facilitate the C-B bond cleavage.^{5, 34} However, these speculated intermediates and their final products have not been experimentally demonstrated.^{5, 7} To elucidate this issue, gas chromatography-mass spectrometry (GC-MS) was employed. When using ethanol as the solvent, besides the desired biphenyl product, the triethyl borate compound was also detected (Figure S24). Besides, the reaction can also be driven by the EtONa compound (Figure S25). Thus, we deduce that the ethoxide (EtO⁻) may interact with phenylboronic acid to form C₆H₅-B(OH)₂EtO⁻ radicals. This hypothesis was theoretically confirmed by DFT calculation

(Table S3). The results show that the C-B bond dissociation energy of $\text{C}_6\text{H}_5\text{-B(OH)}_2\text{EtO}^-$ radicals is $317.48 \text{ kJ mol}^{-1}$, which is lower than that of $\text{C}_6\text{H}_5\text{-B(OH)}_2$ ($468.78 \text{ kJ mol}^{-1}$), and $\text{C}_6\text{H}_5\text{-B(OH)}_2\text{CO}_3^{2-}$ ($325.56 \text{ kJ mol}^{-1}$) and $\text{C}_6\text{H}_5\text{-B(OH)}_3^-$ ($320.79 \text{ kJ mol}^{-1}$), indicating that the EtO^- is more conducive to boost the C-B bond cleavage of phenylboronic acid. Similarly, when using isopropanol and butanol solvents, both biphenyl and boron-alcohol compounds (triisopropyl borate and tributyl borate, Figures S26-29) can be detected. Tributyl borate cannot be detected by GC-MS (Figure S27), even for the pure compound (Figure S28). Instead, Raman measurements confirm the existence of this product in the reaction (Figure S29). These experimental and theoretical results confirmed the key role of alkoxide (R-O^-) like EtO^- in triggering the Suzuki reaction.

To further confirm the proposed reaction mechanism, the catalytic performance in protic solvents (ethanol, isopropanol and butanol) and aprotic solvents (acetonitrile, acetone and dichloromethane) was compared. Figure 3a shows that protic solvents exhibit high activities, while no biphenyl product is detected in aprotic solvents (Figures S30 and S31). However, when ethanol was added to acetonitrile, a measurable conversion was measured (Figure 3b), suggesting the critical role of alkoxide in the Suzuki reaction.^{5, 34} Subsequently, the effects of different bases were examined. Figure 3c shows the reaction could not proceed without a base, as it is necessary to dissociate the alcohols. All carbonate bases are effective, while hydroxide bases yield moderate conversion. This can be attributed to the fact that abundant free and reactive hydroxides interact strongly with Pd, thus covering active sites, leading to the lower catalytic performance.³⁵

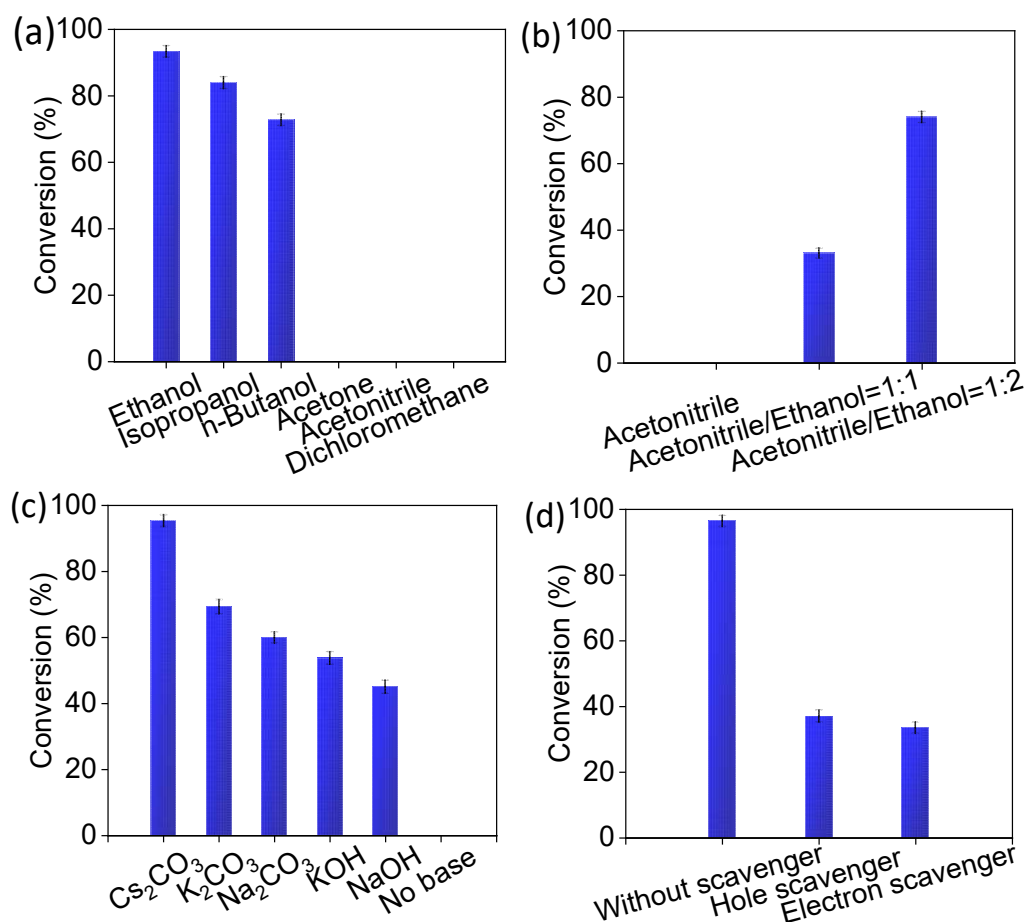


Figure 3. Effects of (a, b) solvents, (c) bases and (d) scavengers on the catalytic activity over 3 wt% Pd/CsPbBr₃. Reaction conditions: 0.1 mmol iodobenzene, 0.12 mmol phenylboronic acid, 15 mg catalyst, 0.4 mmol base, 3 mL solvent, simulated solar light (150 W Xe lamp, AM 1.5G), reaction time (4 h).

Finally, the influence of photoexcited charge carriers on the Suzuki coupling was studied by using scavengers. With electron scavenger 5,5-Dimethyl-1-pyrroline N-oxide,^{3, 7} the conversion is decreased to the same level as no-light conditions (Figure 3d), suggesting that the photon-mediated reaction is quenched. Since ethanol is considered as a holes scavenger, triethanolamine possessing lower oxidation potential than ethanol,³⁶ was employed to trap the holes. A dramatic decrease in the conversion is observed. These results show that the coupling reaction cannot proceed smoothly

without photogenerated electrons and holes. Moreover, no oxidation products of solvents and reduction products (such as H₂) were detected *via* GC and GC-MS measurements (Figures S24, S26-27), indicating that holes were not transferred to the solvent and oxidize it during the reaction process.

Based on above results, we propose a plausible mechanism that is responsible for photothermal catalytic Suzuki couplings over the Pd/CsPbBr₃ catalyst (Equation S1). Under light irradiation, CsPbBr₃ absorbs solar light to produce electron-hole pairs. Electrons transfer to Pd through the Schottky contact,^{3, 4} and the electron-rich Pd can activate the C-X bond of aryl halides and produce Pd-adsorbed aryl.^{19, 37} Meanwhile, phenylboronic acids and alkoxide form a boron-alkoxide complex, where holes assist in the activation of this molecule by weakening the C-B bonds.^{4, 7} These reactions can be more effective due to the reduced activation barrier originating from the photothermal synergistic effect. When the activated phenylboronic acids complex transfers to the redox-activated aryl halides, the coupling reaction occurs easily to produce the desired biphenyl products.

3. Conclusions

In summary, the photothermal and thermal contribution to the catalytic activity and the mechanism of the Suzuki reaction were investigated using a Pd NCs-decorated MHP (Pd/CsPbBr₃) photothermal catalyst. Photo and thermal contributions were derived from the temperature-dependent experiments, showing that light plays a key role at mild conditions (< 30 °C) while thermal catalysis component takes over at higher temperatures. At room temperature, the reduced activation energy of the photothermal processes, results in an over 11 times higher activity for Pd/CsPbBr₃ than for pure CsPbBr₃. Detailed optical and photoelectrochemical studies showed that Pd deposition

not only promotes the separation of photogenerated charge carriers, but it also passivates CsPbBr₃ surface defects. Furthermore, the reaction mechanism of the photocatalytic Suzuki process was experimentally and theoretically demonstrated. This work provides a new perspective to study photothermal catalysis and offers mechanistic insights in the photocatalytic Suzuki reaction.

4. Experimental section

Materials

Lead(II) bromide ($\geq 98\%$), potassium bromide ($\geq 99\%$), L-ascorbic acid (99%), poly(vinyl pyrrolidone) (PVP, M.W. $\approx 55\,000$), cesium carbonate (99.9%), sodium carbonate ($\geq 99.5\%$) potassium carbonate ($\geq 99\%$), sodium hydroxide (98%), potassium hydroxide (pellets for analysis), iodobenzene (98%), phenylboronic acid (95%), acetonitrile ($\geq 99.8\%$), dichloromethane ($\geq 99.8\%$), 4-chlorobiphenyl (99%), 1-chloro-4-iodobenzene (99%), acetaldehyde diethyl acetal (99%), 3-iodoacetophenone (97%), 4-ethoxyphenylboronic acid (99%), 4-tert-butylphenylboronic acid ($\geq 95\%$), 4-iodoacetophenone ($\geq 97\%$), 1-butanol (99.8%) and tributyl borate ($\geq 99\%$) were purchased from Sigma-Aldrich. Ethanol (absolute, $\geq 99.8\%$) and acetone ($\geq 99.8\%$) were purchased from Fisher Chemical. 3-(hydroxymethyl)phenylboronic acid and 1-propanol ($\geq 99.5\%$) were bought from Honeywell. Dimethyl sulfoxide (DMSO, anhydrous, Max. 0.005% water), 2-propanol (99.9%) and toluene (99%) were supplied by VWR chemicals. Cesium bromide (99.9%), potassium palladium(II) chloride (99.9%), 4-(hydroxymethyl)benzeneboronic acid (98%) and trifluorotoluene (99%) were purchased from Alfa Aesar. The Milli-Q water was obtained from the Milli-Q System. All chemicals were used without further purification.

Photocatalyst preparation

Preparation of CsPbBr₃ catalyst

CsPbBr₃ was synthesized at room temperature by the anti-solvent precipitation method.¹² First, lead(II) bromide (PbBr₂) and cesium bromide (CsBr) were dissolved in dimethyl sulfoxide (DMSO) at a precursor concentration of 0.3 M with a molar ratio of 1:1. After the PbBr₂ and CsBr precursors were fully dissolved, the precursor solution was added into toluene solution to get the CsPbBr₃ suspension. Finally, the suspension was dried in a vacuum oven at 70 °C overnight.

Synthesis of palladium nanocubes (Pd NCs)

Palladium nanocubes (Pd NCs) were synthesized according to previous method.¹³ First of all, 105 mg poly(vinyl pyrrolidone) (PVP), 60 mg L-ascorbic acid (AA) and 600 mg of KBr were put in an 8 mL aqueous solution, and pre-heated under magnetic stirring at 80 °C for 10 min. Secondly, 63 mg potassium palladium(II) chloride (K₂PdCl₄) was dissolved in 3.0 mL aqueous solution, then the K₂PdCl₄ solution was added into the above solution and kept stirring at 80 °C for 3 h, where PVP, AA and KBr acted as a stabilizer, reductant, capping agent, respectively. Finally, the Pd NCs product was collected by centrifugation and washed with ethanol, and re-dispersed in ethanol at a concentration of 1 mg/mL.

Fabrication of Pd/CsPbBr₃ composites

A series of x wt% Pd/CsPbBr₃ catalysts were synthesized at room temperature by the similar precipitation method mentioned above. In a typical experiment (3 wt% Pd/CsPbBr₃), 100 mg CsPbBr₃ powder was first added to 15 mL ethanol solution and kept stirring for 30 min. After that, 20 mL of ethanol solution containing 3 mg Pd NCs

was added dropwise into the vigorously stirred CsPbBr₃ suspension. Then the mixture was kept stirring at room temperature for 12 h. Finally, the Pd/CsPbBr₃ suspension was collected by centrifugation and dried in a vacuum oven at 70 °C.

Characterization

X-ray diffraction (XRD) patterns of the samples were recorded with a Malvern PANalytical Empyrean diffractometer with Bragg-Brentano geometry, using a PIXcel3D solid-state detector and a Cu anode, and the diffractogram was recorded in the 2 θ ranging from 10 to 70 degrees with a step size of 0.0131° and an integration time of 150 s/step. For the temperature-dependent XRD patterns, the diffractometer was equipped with an Anton Paar TTK 600 low-temperature chamber with a CCU 100 control unit as the heating stage. The temperature was varied from 30 °C up to 60 °C. Each diffractogram was recorded every 10 °C where the chosen temperature was kept for 5 min before the measurement. The sample was deposited as a powder bed and heated at 10°C/min in N₂. Ultraviolet-visible spectrophotometer (UV-Vis, Lambda-950) was employed to obtain the optical properties of the samples by UV-vis diffuse reflectance spectroscopy (DRS) in the wavelength 300-800 nm with 1 nm increment, where BaSO₄ and black carbon were used as the references. Scanning electron micrographs of samples were recorded by scanning electron microscopy (SEM, FEI-Q FEG250). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were analysed using a JEOL model JEM 2010 EX instrument at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS, Al K α X-ray source, 1486.6 eV) was employed to investigate the chemical structure and valence state of the elements of the catalysts, and the C 1s signal was set to a position of 284.6 eV. Electrochemical impedance spectroscopy, cathodic

polarization curves and photocurrent response, were made using a standard three-electrode setup. Ag/AgCl electrode was employed as the reference electrode, and a platinum sheet was used as the counter electrode. The working electrode was deposited on a cleaned indium tin oxide (ITO) substrate. More specifically, firstly, 10 mg powder photocatalyst was fully dispersed in 1 mL toluene by sonication. Then 20 μ L slurry solution was dropped onto the ITO substrate where the exposed area of the working electrode was fixed at 0.25 cm² by using Scotch tape to protect the boundary of the ITO substrate, and dried at 80 °C for 2 h to improve adhesion. After that, the Scotch tape was unstuck, followed by isolating the uncoated electrode with epoxy resin. Connection to the CsPbBr₃ working electrode was immersed in the electrolyte solution. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in dichloromethane (DCM) solution was used as the electrolyte. Electrochemical impedance spectra were obtained on an electrochemical workstation by applying an alternating current (AC) voltage (5 mV amplitude) in a frequency range from 10 KHz to 5 MHz with the open circuit potential of 0.2 V under simulated solar light. Photocurrent response measurements were performed as that of impedance spectra. Cathodic polarization curves were achieved via linear sweep voltammetry technique with a scan rate of 0.2 mV/s. Raman measurements were performed using an upright optical microscope (BX53, Olympus, Japan) equipped with a motorized stage (Märzhäuser Wetzlar GmbH, Germany) on a commercial Raman setup (MonoVista CRS+, S&I GmbH, Germany). Continuous-wave laser light from 785 nm laser (IPS, USA) with an average power of 5 mW was focused onto the sample with a 50x objective (MPLN, Olympus, Japan). After collecting light by the same objective, the Raman scattered light from the sample was filtered using a long-pass edge filter (LP02-785RE-25, Semrock, USA) and passed through a 100 μ m confocal pinhole. Afterwards, the signal is sent to a monochromator

(SpectraPro HRS-500, Princeton Instruments, USA) equipped with a grating of 1200 grooves/mm. The signal is then directed to a CCD camera (Newton 920, Andor, UK) for recording. The measurements at different temperatures were performed using a temperature-controlled stage (Linkam Scientific Instruments, UK). The acquisition time was set to 1 s with averages of 5 acquisitions to increase the signal-to-noise ratio. For the temperature-dependent photoluminescence (PL) measurements, a He flow cryostat in which the temperature can be varied from 4.2 to 300 K was used. The sample was excited with a solid-state laser (Thorlabs M365LP1 with driver DC2200) operating at 365 nm *via* a 550 μm core optical fiber. The PL spectra were collected in an increment of 5 K through 11 optical fibers surrounding the excitation fiber. The fibers were coupled to a LOT-QD Shamrock F/4 spectrometer with an electron-multiplying charge-coupled detector iXon DV887. Time-resolved PL spectra were recorded on a Leica DMI8 system. As an excitation source, a pulsed white light laser (SuperK Extreme EXW-12, NKT Photonics) operating at 405 nm and set at a repetition rate of 20 MHz and a fluence of $2 \mu\text{J mm}^{-2}$ was employed. The samples were mounted on a Linkam stage where the temperature can be varied between room temperature and 500 K. The samples were illuminated through an air objective of an inverted microscope system (Leica DMI8). The fluorescence photons were detected by an avalanche photodiode (SPCM-AQR-14, Perkin-Elmer) *via* the same objective passing through dichroic and cut-off filters. Photon counting and time tagging were performed within a TimeHarp 200 module (PicoQuant), with a time resolution of 29 ps per channel. The fluorescence lifetime images were analyzed using SymphoTime 32 software (PicoQuant). All calculations were carried out with the Gaussian 16 program. The B3LYP/6-311+G(3df,2p) was used for all geometry optimizations, vibrational

frequency and single-point energy calculations.

(Photo)thermal catalytic coupling reaction

All Suzuki cross-coupling reactions were conducted in a 25 mL quartz reactor. In a typical experiment, 0.1 mmol iodobenzene, 0.12 mmol phenylboronic acid, 0.4 mmol Cs₂CO₃ and 15 mg catalyst were mixed in 3 mL ethanol, then the reactant mixture and solvent were evacuated by a mechanical pump to remove air completely and protected by an Ar atmosphere before irradiation. The mixture was stirred continuously under 1-sun solar irradiation (AM 1.5G) with a 150 W Xe lamp for 4 h. The temperature of the reaction system was accurately controlled within the temperature window 5-60 °C and kept 1-sun solar light intensity. After the reaction, the mixture was centrifuged, and the filtrates were analyzed by GC to obtain the conversion of iodobenzene. The conversion and selectivity of iodobenzene were defined as follows:

$$\text{Conversion (\%)} = [(C_0 - C_A)/C_0] \times 100\%$$

$$\text{Selectivity (\%)} = [C_B/(C_0 - C_A)] \times 100\%$$

Where C₀ is the initial concentration of iodobenzene, C_A and C_B are the concentrations of the iodobenzene and corresponding product of the reaction, respectively.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/>

SEM, XRD, TEM, Raman, PL, TRPL, BET, XPS, GC-MS, absorption spectra, recycle test, apparent activation energy, surface charge transfer efficiency (η_t), bond dissociation energy, and comparison of catalytic performance.

Author contributions

C.W. and B.W. conceived the science, and C.W. conducted the experiments. M.K. performed the PL measurements. H.H. recorded the TEM data. M.Y., Y.D. and B.L.S. carried out XPS, ICP-MS and photoelectrochemical measurements. I.A. and G.R. assisted with Raman and XRD experiments. F.L., H.J. and J.A.S. supported the experiments and data analysis. C.W., B.W., J.H. and M.B.J.R. wrote the manuscript. All authors have approved the manuscript.

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Notes

The authors declare no competing financial interest.

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