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## An effective photothermal dual-responsive Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> catalyst for Suzuki–Miyaura coupling reaction under mild conditions

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The Suzuki–Miyaura coupling reaction is one of the effective methods for forming C-C bonds in modern organic synthesis. However, most of the current catalysts can only effectively catalyze the aryl iodides and aryl bromides, and the catalytic activity for the inexpensive aryl chlorides is relatively low. Herein, the  $Pd_1Cu_4/Ce_xO_y$  catalysts can not only exhibit excellent performance in the conventional thermal reactions of aryl bromides and arylboronic acids, but also effectively activate aryl chlorides in Suzuki-Miyaura coupling reactions under the visible light irradiation at room temperature. The  $Ce_xO_y$  carriers can provide photogenerated electrons to enrich the electron density of the Pd nanoparticles, which can effectively activate the strong C-Cl bonds of the aryl chlorides. Meanwhile, the photogenerated holes of  $Ce_xO_y$  catalysts prepared in this work could provide a great promise for using inexpensive metals to synergistically catalyze the Suzuki-Miyaura coupling reactions.

## 1. Introduction

The Suzuki-Miyaura (SM) coupling reaction is one of the effective methods for forming C-C bonds in modern organic synthesis, so it is widely used in theoretical research and industrial production.<sup>1-5</sup> The reaction generally employs an arylboronic acid and an aryl halide as a substrate. Among the aryl halides, aryl iodides and aryl bromides have higher activity, and aryl chlorides are difficult to be activated due to the presence of strong C-Cl bonds, so aryl iodides and aryl bromides usually used in SM coupling reactions.<sup>6-10</sup> Metal palladium and its oxidation are the most efficient and commonly used catalytic materials for SM coupling reactions.<sup>11-14</sup> However, since the price of the precious metal is relatively high, it is desirable to reduce the amount of palladium by introducing a part of the inexpensive metal, and to synergize with the palladium in the reactions.

Copper metal and its compounds are the most low-cost materials among the commonly used catalysts for the reactions such as Pd, Ni and their compounds. Therefore, from the economical point of view, Cu could be employed as a synergistically catalyzed metal.<sup>15-20</sup> Among various compounds of Cu, cuprous oxide is inexpensive, low toxicity, and high catalytic activity in the carbon-carbon coupling reactions. The

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59 60 application of cuprous oxide for this reaction has been the focus of organic chemists and played an important role in the development of green chemistry.21-23 Therefore, the use of cuprous oxide as a synergistic catalyst for palladium is a viable solution. However, it is worth to notice that most catalysts which are currently used in the SM coupling reactions are hot catalysts. Their catalytic activities on the aryl iodide and aryl bromide are relatively high, but still not satisfy the reactions when used inexpensive aryl chloride as the substrate.24, 25 A viable solution for the problems above mentioned is to promote the oxidative addition step of the SM coupling reaction by enriching the electron density of the catalytic active center, thereby achieve the activation of the aryl chloride under a mild condition. A photocatalytic method in which photogenerated electrons are injected into Pd nanoparticles under visible light irradiation can effectively enrich the electron density of Pd nanoparticles. For example, Sun et al. synthesized Au-Pd nanostructures and demonstrated that the Au nanocrystal core acts as a plasmonic component for efficient light absorption, and the Pd nanoparticles act as SM reactions.<sup>26</sup> the catalysts for Moreover, the photogenerated electrons of the SiC surface and excited electrons of the Cu particles in the PdCu alloy could be transferred to Pd under light irradiation, which was confirmed by Wang et al.<sup>27</sup> In recent years, the application of rare earth oxides as photocatalysts to various chemical reactions has become a research hotspot. Among them, resource-rich and inexpensive cerium oxide is widely used as a carrier material in heterogeneous catalysis.<sup>28-32</sup> Although the band gap of cerium oxide is very wide, the precious metal Pd and the Cu<sub>2</sub>O

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semiconductor with narrow band gap can effectively improve the visible light absorption range of the composite material,<sup>33-</sup> <sup>36</sup> and suppress the recombination of photogenerated electrons and hole pairs, thereby effectively utilizing them under visible light irradiation,<sup>37,38</sup> In addition, the cerium element has a ground state electron ([Xe]4f<sup>1</sup>5d<sup>1</sup>6s<sup>2</sup>) in the 4f orbital, which gives cerium oxide excellent redox characteristics. As the most common lattice defects, oxygen vacancies of cerium oxide can also enhance its redox properties.<sup>39-42</sup> These properties of cerium oxide are extremely important for the SM coupling reactions.

In this work, Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> composite was prepared by electrospinning, high temperature calcination, and hydrogenation reduction. The morphologies and components of the composite were characterized by FE-SEM, TEM, TGA, XRD, XPS, BET and ICP. Its catalytic performance was evaluated for SM coupling reaction. This composite can not only exhibit excellent performance in the conventional thermal reactions of aryl bromides and arylboronic acids, but also effectively activated aryl chlorides under visible light irradiation at room temperature.

## 2. Experimental

#### 2.1. Chemicals

Palladium chloride (Pd  $\geq$  59%), Copper Chloride Dihydrate (99.0%), N, N-Dimethylformamide (DMF, 99.5%), Anhydrous ethanol (99.7%), Bromobenzene (99.5%) and Chlorobenzene (99.5%) were obtained from Sinopharm Chemical Reagent Co.,Ltd. Polyvinylpyrrolidone (PVP, Mw = 1, 390, 000) was purchased from Gobrkie New Material Technology Co.,Ltd. Cerium nitrate (99.0%) was provided from Tianjin Xingfu Fine Chemical Research Institute.

#### 2.2 Catalyst Preparation

The  $Pd_1Cu_4/Ce_xO_y$ catalysts were fabricated via electrospinning, high temperature calcination and hydrogenation reduction methods. In a typical experiment, 0.018 g of  $PdCl_2$  and 0.069 g of  $CuCl_2 \cdot 2H_2O$  were first added to 1.35 g of ethanol and 20.25 g of DMF mixed solution, which was stirred continuously for 8 h. Then, 1.35 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 2.25 g of PVP were put into the above solution by stirring for 12 h to obtain the precursor solution. The precursor solution was prepared into nanofibers by electrospinning at 20 cm distance and 15 kV voltages. The nanofibers were placed in a tube furnace and raised to 250 °C at a heating rate of 5 °C/min under air atmosphere for 3 h, and then heated to 500 °C for 4 h. Finally, the calcined samples were hydrogenated at a pressure of 3 MPa and a temperature of 120  $^\circ C$  for 12h to achieve the  $Pd_1Cu_4/Ce_xO_y$  catalysts.

#### 2.3 Catalyst characterization

The transmission electron microscope (TEM) and high resolution transmission electron microscopy (HRTEM) images of the samples were taken by JEM-2100 (JEOL, Japan). The surface morphological characterization of the samples was

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examined by field emission scanning electron microscopy (FE-SEM, FEGQUANTAN 650). The crystal structure of the crystal of the composites was characterized by X-ray Diffractomer (XRD, D/Max-2500). The instrument was equipped with Cu-Ka radiation and the range of 20 angle was from 5° to 90°. The Xray photoelectron spectroscopy (XPS, Escalab 250xi) was used to determine the elemental composition, content and chemical state of the samples. Thermogravimetric Analysis (TGA, STA449 F3) was used to observe the weight change of the samples with increasing temperature. The absorption capacity of different catalysts for visible light was detected by Ultraviolet-visible Spectrophotometer (UV-vis, SHIMADZU, UV-2700). The specific surface areas and poresizes of the samples were calculated by Brumauer-Emmett-Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The content of Pd in the samples was detected by Agilent ICP-OES 730. The gas chromatograph (GC, SHIMADZU, GC-2010) was employed to analyze the yield of the products in the SM coupling reactions.

#### 2.4 Catalytic Activity Measurement

The  $Pd_1Cu_4/Ce_xO_y$  catalysts were employed in SM coupling reactions to evaluate the catalytic activity. Typically, aryl halides, arylboronic acids, bases and the catalysts were added to the mixed solution of EtOH/H<sub>2</sub>O. After the reactions, the solution was added into a separatory funnel containing ethyl acetate and distilled water for extraction. The organic layer solution was detected by GC and the yield of the products was calculated. The catalysts were separated by centrifugation and washed several times with ethanol and distilled water, and then dried for subsequent cycle reactions.

## 3. Results and discussion

To investigate the relationship between sample weight and temperature change, the TG analysis of PdCl<sub>2</sub>-CuCl<sub>2</sub>-Ce(NO<sub>3</sub>)<sub>3</sub>/PVP nanofibers is performed under the analytical condition for TGA is from 45 °C to 800 °C at a heating rate of 10 °C/min. The results are shown in Fig. 1. There are three stages in weight loss in the air. When the temperature raises from 50 °C to 274 °C, the weight loss of the sample is about 14.57% which belongs the crystal water of CuCl<sub>2</sub>·2H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. On the second step, due to the massive decomposition of PVP, the dramatic weight loss of the sample which is about 23.15% occurs between the the temperature ranging from 274°C to 276 °C. With the temperature increasing from 276 °C to 420 °C, the weight loss is 47.03%, which is because of the decomposition of the cerium nitrate and the residual PVP. The results indicate that the calcination temperature of the catalysts in the tube furnace is determined to be 500 °C.

The morphologies of the samples are observed by the FE-SEM, as the Fig. 2 shows. In Fig. 2a, A smooth surface is found on the PdCl<sub>2</sub>-CuCl<sub>2</sub>-Ce(NO<sub>3</sub>)<sub>3</sub>/PVP nanofibers with diameters ranging from 200 nm to 300 nm. The FE-SEM images also show that after the high temperature calcination and hydrogenation reduction (Fig. 2b), the surface wrinkled coaxial Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> nanotublular structure is obtained. This structure is beneficial

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Fig. 1 TGA curves of PdCl<sub>2</sub>-CuCl<sub>2</sub>-Ce(NO<sub>3</sub>)<sub>3</sub>/PVP nanofibers.

to the increasing of the specific surface area. In comparison with the initial electrospinning fibers in Fig. 2a, the diameters of the  $Pd_1Cu_4/Ce_xO_y$  samples are slightly reduced because the PVP is removed during the high temperature calcination.

To further observe the morphologies of the samples, the TEM images are obtained. As can be seen from Fig. 2c and d, the coaxial nanotubular structure can be clearly observed. Moreover, granular and rugged surfaces are found in Fig. 2e, which indicates the increasing of the specific surface area of the samples, and more active site exposure compared with the smooth surfaces. In addition, the HRTEM image is obtained, as shown in Fig. 2f, the nanoparticles with the lattice spacing of 0.20nm, 0.21nm, 0.23nm and 0.32nm are corresponding to the PdO (102) plane, Cu<sub>2</sub>O (100) plane, Pd (111) plane and CeO<sub>2</sub> (111) plane, respectively, indicating the Pd/PdO,  $Cu_2O$  and  $CeO_2$  of the  $Pd_1Cu_4/Ce_xO_y$  have good crystallinity. As is seen from the element mapping images of  $Pd_1Cu_4/Ce_xO_y$ , the Pd and Cu clusters supported on  $Ce_xO_y$  are evenly distributed. The ICP-OES results of the  $Pd_1Cu_4/Ce_xO_y$  are



Fig. 2 FE-SEM images of  $PdCl_2$ -CuCl\_2-Ce(NO<sub>3</sub>)<sub>3</sub>/PVP (a) and  $Pd_1Cu_4/Ce_xO_y$  (b), TEM images of  $Pd_1Cu_4/Ce_xO_v$  (c,d,e), HRTEM image of  $Pd_1Cu_4/Ce_xO_v$  (f) and element mapping images of Pd, Cu, Ce and O for the Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub>.

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shown in Table S1.

View Article Online The specific surface area and pore size distribution 3001056 samples are analyzed by BET and BJH calculation methods. The N<sub>2</sub> physisorption isotherm of the samples is shown in Fig. 3a, we can observe that it is a type IV isotherm curve. The samples exhibit double hysteresis loops in the isotherm ranging from  $P/P_0 = 0.35$  to 0.85 and from 0.85 to 0.98, which may be due to the different pore structures of the inner and outer nanotubes. The specific surface area of the samples can be calculated by the BET analysis which is 91 m<sup>2</sup>/g. The pore sized distribution profiles of the samples are presented in Fig. 3b, the average pore diameter of the samples calculated by the BJH analysis is 16 nm, indicating that the samples are mesoporous materials. The high specific surface area and large pore size can expose more active sites and increase the contact area with the substrate, thereby enhance the catalytic activity of  $Pd_1Cu_4/Ce_xO_y$ .

The XRD pattern of the  $Pd_1Cu_4/Ce_xO_y$  is shown in Fig. 4a. The diffraction peaks at 20 = 28.5°, 33.0°, 47.5°, 56.2°, 69.3°, 76.9°, 78.8°, and 88.3° are corresponding to the crystal faces of (111), (200), (220), (311), (222), (400), (331), (420) and (422) of cubic fluorite CeO<sub>2</sub> (JCPDS 43-1002), respectively, indicating a high quality of crystallinity in CeO<sub>2</sub> nanotubes. The diffraction peaks of Pd and Cu are not detected because of their low contents. The Ce 3d XPS spectrum is shown in Fig. 4b, the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> spin-orbital components are represented by V and U respectively. The V'/U' component is the feature of  $Ce^{+3}$  and the V/U, V"/U", and V"'/U" components are the features of  $Ce^{+4}$ . These results confirm that the  $Ce_xO_y$  has a mixed valence, and the atomic ratio of Ce<sup>+3</sup>/Ce<sup>+4</sup> is 0.31 which is calculated by the peak area ratio. The presence of Ce<sup>+3</sup> is advantaged to increase the oxygen vacancy of  $Ce_xO_y$ , which promotes the redox in SM coupling reactions. As shown in Fig. 4c, the binding energies of Cu in  $Pd_1Cu_4/Ce_xO_y$  are 952.1 eV for Cu 2p<sub>1/2</sub> and 932.3 eV for Cu 2p<sub>3/2</sub>. Due to the binding energies of Cu<sup>0</sup> and Cu<sup>+1</sup>are around 951.9 eV, 932.4eV and 952.4eV, 932.7eV respectively, the Cu<sup>0</sup> and Cu<sup>+1</sup> cannot only be distinguished by using the XPS spectrum. Hence, we further investigate the state of Cu by the Auger electron spectrum. The inset of Fig. 4c shows the binding energy of the Auger peak is around 570 eV which corresponds to Cu<sub>2</sub>O. The Pd 3d XPS spectrum is shown in Fig. 4d, there are two states of the Pd species. The binding energies of Pd<sup>+2</sup> are 342.5 eV for Pd 3d<sub>3/2</sub> and 337.2 eV for Pd 3d<sub>5/2</sub>, respectively. Similarly, the binding energies of 340.2 eV and 335.0 eV belong to Pd<sup>0</sup>. The percentage contents of PdO and Pd are 73% and 27%,



Fig. 3  $N_2$  adsorption-desorption isotherms (a) and pore size distribution curves (b) of Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub>.

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Fig. 4 XRD pattern of  $Pd_1Cu_4/Ce_xO_y$  (a), XPS spectra of  $Ce_xO_y$  (b), Cu (c), Pd (d) in  $Pd_1Cu_4/Ce_xO_y$ . The inset in (c) is the Auger electron spectrum of Cu in  $Pd_1Cu_4/Ce_xO_y$ .

respectively. It demonstrates that PdO is the major part of the Pd/PdO catalytic active center.

In Fig. 5, the effect of different reaction conditions on biphenyl yield is investigated. The yield of biphenyl increases from 91% to 99% in a shorter time range from 10 minutes to 30 minutes, indicating that the  $Pd_1Cu_4/Ce_xO_y$  catalysts have an excellent catalytic efficiency in the reactions of bromobenzene with phenylboronic acid (Fig. 5a). Then the effect of temperature on biphenyl yield is studied (Fig. 5b). When the temperature rises from 25 °C to 70 °C, the yield of biphenyl is



**Fig. 5** (a) The time course of biphenyl yield by  $Pd_1Cu_4/Ce_xO_y$  catalysts. Reaction conditions: 1 mmol of bromobenzene, 1.2 mmol of phenylboronic, 1mg of catalysts, 3 mL of water, 4 mL of alcohol, 1.5 mmol of sodium hydroxide, 70 °C. (b) The effect of temperature variation on biphenyl yield. Reaction conditions: 1 mmol of bromobenzene, 1.2 mmol of phenylboronic, 1mg of catalysts, 3 mL of water, 4 mL of alcohol, 1.5 mmol of sodium hydroxide, 30 min. (c) The effect of different bases on biphenyl yield. (d) Recycling experiments of the  $Pd_1Cu_4/Ce_xO_y$  catalysts in the reactions of bromobenzene with phenylboronic acid.

increasing. However, the yield does not change when the temperature rises to 80 °C. The effect of various bases in the



**Fig. 6** The effect of various catalysts on biphenyl yield. Reaction conditions: 1 mmol of bromobenzene, 1.2 mmol of phenylboronic, 1mg of catalysts, 3 mL of water, 4 mL of alcohol, 1.5 mmol of sodium hydroxide, 30 min, 70 °C.

reactions is shown in Figure 5c. It can be observed from the results that inorganic bases can be more effective than the organic bases in the reactions. Among the inorganic bases, the NaOH and KOH are the stronger ones which can enhance the yield. The recycling results of the reactions are shown in Fig. 5d. After five cycles of the reactions, the catalysts can still maintain their excellent catalytic performance, which proves that they have a good stability.

In comparison of the  $Pd_1Cu_4/Ce_xO_y$  and  $Pd_1Cu_4/CNF$ ,  $Pd_1Cu_4/Ce_xO_y$  catalyst displayed a better catalytic performance in the reactions of bromobenzene with phenylboronic acid, as shown in Fig. 6, this may be due to the  $Ce_xO_y$  has a higher specific surface area and richer oxygen vacancies than CNFs. Moreover, the catalytic performances of  $Pd_1/Ce_xO_y$  and  $Cu_4/Ce_xO_y$  are also investigated. The yields of biphenyl in the reactions catalyzed by the  $Pd_1/Ce_xO_y$  and the  $Cu_4/Ce_xO_y$  were 85% and 3%, respectively. However, the yields of biphenyl employing the  $Pd_1Cu_4/Ce_xO_y$  catalysts in the reactions are 99%, which proves that  $Cu_2O$  acts synergistically with Pd. When the content of Cu continues to increase, we can observe the yields of biphenyl degradation of the  $Pd_1Cu_8/Ce_xO_y$  catalysts.

Additionally, we investigate the catalytic activities of the  $Pd_1Cu_4/Ce_xO_y$  in the reactions of chlorobenzene with phenylboronic acid. In Fig. 7a, curve A shows the time course of biphenyl yield in the thermal reactions of chlorobenzene with phenylboronic acid. Due to the strong chemical inertness of the C-Cl bonds, we can observe that the reactions at 70 °C for 6 h, the yield of biphenyl is still low (< 20%). In order to activate the strong C-Cl bonds, we introduce the visible light irradiation. The time course of biphenyl yield in the reactions of chlorobenzene with phenylboronic acid under visible light irradiation is shown in the curve B. The biphenyl yield is greatly improved indicating that the photogenerated electrons can effectively activate the C-Cl bond under a visible light irradiation. The catalysts can keep a high activity and good crystalline structure after five cycles of reactions (Fig. 7d and S1). As can be seen from Fig. 8a and b, after five cycles, the morphology of the catalysts is not destroyed, and the nanoparticles on carriers have no obvious agglomeration.

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**Fig. 7** (a) The time course of biphenyl yield by  $Pd_1Cu_4/Ce_xO_y$  catalysts. A Reaction conditions: 0.25mmol of chlorobenzene, 0.3mmol of phenylboronic acid, 20mg of catalysts, 1 mL of water, 2 mL of alcohol, 0.375 mmol of sodium hydroxide, 70 °C. <sup>B</sup>Reaction conditions: 0.25mmol of chlorobenzene, 0.3mmol of phenylboronic acid, 20mg of catalysts, 1 mL of water, 2 mL of alcohol, 0.375 mmol of sodium hydroxide, room temperature, visible light. (b) UV-vis absorption spectra of various catalysts. (c) The effect of various catalysts on biphenyl yield. Reaction conditions: 0.25mmol of chlorobenzene, 0.3mmol of catalysts, 1 mL of water, 2 mL of alcohol, 0.375 mmol of sodium hydroxide, room temperature, visible light (b) UV-vis absorption spectra of various catalysts. (c) The effect of various catalysts on biphenyl yield. Reaction conditions: 0.25mmol of chlorobenzene, 0.3mmol of phenylboronic acid, 20mg of catalysts, 1 mL of water, 2 mL of alcohol, 0.375 mmol of sodium hydroxide, room temperature, visible light, 6h. (d) Reusability study of the Pd\_1Cu\_4/Ce\_xO<sub>y</sub> catalysts in the reactions of chlorobenzene with phenylboronic acid under visible light irradiation.

The UV-vis absorption spectra of various catalysts are shown in Fig. 7b. The visible light absorption range of pure Ce<sub>x</sub>O<sub>y</sub> is around 400-425 nm. As can be seen from Fig. 7b, a red-shift occurs in the absorption spectrum of  $Ce_xO_y$ , because the energy band structure of the  $Ce_xO_y$  semiconductor is changed after the introduction of noble metal Pd. Owing to the narrow-band gap Cu<sub>2</sub>O semiconductor is loaded on the wide-band gap  $Ce_xO_y$ , the sensitization of the  $Cu_2O$  to the Ce<sub>x</sub>O<sub>y</sub> can expand the absorption range of visible light. Therefore, due to the presence of the noble metal Pd and the semiconductor Cu<sub>2</sub>O, the visible light absorption range of the Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> is tremendously improved. The synergy of various components in  $Pd_1Cu_4/Ce_xO_y$  catalysts for the reactions under visible light irradiation is also investigated by employing  $Pd_1/Ce_xO_y$ ,  $Cu_4/Ce_xO_y$ ,  $Pd_1Cu_4/Ce_xO_y$  and  $Pd_1Cu_4/CNF$  as catalysts (Fig. 7c). Despite the Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> catalysts have a little activity in the thermal reactions of bromobenzene with phenylboronic acid at 70 °C (Fig. 6), they can still activate the strong C-Cl bonds of chlorobenzene under visible light irradiation. Meanwhile, Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> exhibits a better catalytic performance than Pd1/CexOy in the reactions, indicating the synergistic effect of Cu<sub>2</sub>O. By comparing the catalytic performance of  $Pd_1Cu_4/Ce_xO_y$  and  $Pd_1Cu_4/CNF$ , it is confirmed the  $Ce_xO_y$  carrier is essential to the SM coupling reactions when they are under visible light irradiation.

To further demonstrate the promotion of photogenerated electrons and holes in the reactions of chlorobenzene with phenylboronic acid, various amounts of electron scavenger KBrO<sub>3</sub> and hole scavenger MeOH are added to the reactions. As shown in Table 1, no biphenyl product is obtained in the

reactions at the room temperature in dark. When wisible light is introduced, the yield of biphenyl achieves more than 99%. After adding 0.25mmol of KBrO<sub>3</sub>, the yield of biphenyl decreases slightly from 99% to 94%. These demonstrate that the presence of photogenerated electrons in the catalysts can promote the reactions. While the amount of KBrO<sub>3</sub> increases to 2.5mmol, the yield of biphenyl is only 8%, which indicates that when the photogenerated electrons are removed, Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> exhibits no catalytic activity in the reactions even under the visible light irradiation. Additionally, to determine whether the KBrO<sub>3</sub> could destroy the catalysts, the catalyst

Table 1 The capture experiment of photogenerated electrons and holes.								
Entry	Visible light	KBrO₃ (mmol)	MeOH (mL)	Yield (%)				
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2	+			99				
3	+	0.25		94				
4	+			8				
5	+			97				
6	+		0.5	86				
7	+		2	44				

Reaction conditions: 0.25mmol of chlorobenzene, 0.3mmol of phenylboronic acid, 20mg of catalysts, 1 mL of water, 2 mL of alcohol, 0.375 mmol of sodium hydroxide, room temperature, 6h.

system after removing KBrO3 has been employed to the



Fig. 8 (a) FE-SEM images and (b) TEM images of five cycle experiments.

reactions, and the yield of biphenyl can recover to more than 97%. This indicates that the presence of  $KBrO_3$  will not destroy the catalysts.

Then the effect of photogenerated holes is also studied. Arylboronic acid can combine with OH<sup>-</sup> in the basic environment and then be adsorbed on the basic sites of  $Ce_xO_y$ . When the photogenerated holes are diffused to the basic sites, the adsorbed molecules can be oxidized with the cleavage of C-B bond.<sup>43</sup> The role of photogenerated holes in the reaction is

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 Table 2 Scope of  $Pd_1Cu_4/Ce_xO_y$  catalysts for the SM coupling reactions

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Entry	Aryl halide	Arylboronic acid	Product	Yield (%)	TOF (h-1)		
1ª	Br	B(OH) <sub>2</sub>		99	12,276		
2ª	Br	B(OH)2		99	12,276		
3ª		B(OH) <sub>2</sub>		76	9424		
4ª	Br			99	12,276		
5ª	Br	H <sub>3</sub> CO B(OH) <sub>2</sub>	H <sub>3</sub> CO	97	12,028		
6 <sup>b</sup>		B(OH) <sub>2</sub>		99	12,276		
7 <sup>b</sup>		B(OH) <sub>2</sub>		99	12,276		
8 <sup>b</sup>	H <sub>3</sub> CO-CI	B(OH) <sub>2</sub>	н <sub>3</sub> со-	78	9673		
9 <sup>b</sup>		B(OH)2	$\checkmark - \bigcirc$	99	12,276		
10 <sup>b</sup>	O <sub>2</sub> N-Cl	B(OH) <sub>2</sub>	0 <sub>2</sub> N-	53	6572		

<sup>a</sup>Reaction conditions: 1 mmol of bromobenzene, 1.2 mmol of phenylboronic, 1mg of catalysts, 3 mL of water, 4 mL of alcohol, 1.5 mmol of sodium hydroxide, 70 °C, 30min. <sup>b</sup>Reaction conditions: 0.25mmol of chlorobenzene, 0.3mmol of phenylboronic acid, 20mg of catalysts, 1 mL of water, 2 mL of alcohol, 0.375 mmol of sodium hydroxide, room temperature, visible light, 6h.

demonstrated by the introduction of methanol as a hole scavenger. The yield of biphenyl decreased from 99% to 86% and 44% after adding 0.5 and 2 mL methanol, respectively,

which indicates that the photogenerated holes can effectively activate the arylboronic acid.

The reaction substrates are further extended to various aryl halides and arylboronic acids to determine the scope of

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coupling reactions under visible light irradiation. reaction systems catalyzed by  $Pd_1Cu_4/Ce_xO_y$  (Table 2). It can be

observed from the results that the  $Pd_1Cu_4/Ce_xO_y$  catalysts have a good universality for the most of the substrates. However, since there are strong electron-withdrawing groups on aryl halide including -OCH<sub>3</sub> (Entry 3<sup>a</sup>, Entry 8<sup>b</sup>) and-NO<sub>2</sub> (Entry 10<sup>b</sup>), the yields of the products can only reach 76%, 78% and 53%, respectively. The 1H NMR and 13C NMR spectra of all the products are provided in supporting information.

The proposed catalytic mechanism is shown in Scheme 1. The presence of Pd and Cu<sub>2</sub>O can expand the visible light absorption range of Ce<sub>x</sub>O<sub>y</sub>, further promote its production of photogenerated electrons, and thereby enrich the electron density of Pd nanoparticles. The Pd nanoparticles with high electron density can effectively activate the aryl halides and promote the oxidative addition reactions by accelerating the formation of the ligand ArPd<sup>II</sup>X.<sup>26</sup> Meanwhile, the arylboronic acids can also be activated by photogenerated holes of Ce<sub>x</sub>O<sub>y</sub>.<sup>43</sup> When the oxidized arylboronic acids meet with the activated aryl halides, the final products of the coupling reactions are obtained.

## 4. Conclusions

In conclusion, the  $Pd_1Cu_4/Ce_xO_y$  can not only exhibit excellent catalytic performance in the thermal reactions of aryl bromides and arylboronic acids, but also effectively activate aryl chlorides for SM coupling reactions under the visible light irradiation at room temperature. The synergy of each component in the catalysts contributes to the activation of reactants. The high specific surface areas and abundant oxygen vacancies of the Ce<sub>x</sub>O<sub>y</sub> nanotubes can promote the redox reactions. Moreover, the presence of Pd and Cu<sub>2</sub>O enhance the visible light absorption of the CexOy, further promote its photogenerated electron generation, then enrich the electron density of Pd nanoparticles. The electron-rich Pd nanoparticles can activate strong C-Cl bonds of aryl chlorides. Meanwhile, the arylboronic acids can also be activated by the photogenerated holes of Ce<sub>x</sub>O<sub>y</sub>. The roles of photogenerated electrons and holes in the reactions are also demonstrated by

the capture experiments. The final products are rectioned when the activated aryl chlorides meep with 3416 3616260 arylboronic acids. The Pd<sub>1</sub>Cu<sub>4</sub>/Ce<sub>x</sub>O<sub>y</sub> catalysts are of great significance in the use of inexpensive metals to synergistically catalyze the SM coupling reactions under the mild conditions.

## **Conflicts of interest**

There are no conflicts to declare.

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The  $Pd_1Cu_4/Ce_xO_y$  catalysts can efficiently catalyze the Suzuki reactions under both heating and visible light irradiation conditions.