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# Pd Nanoparticles immobilized on *individual calcium carbonate plate* derived from mussel shell waste: An eco-friendly catalyst for copper-free Sonogashira coupling reaction

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Abstract: Conversion of waste into high value materials has been considered an important sustainability strategy in modern chemical industries. Large volume of shell waste is generated globally from mussel cultivation. In this work, mussel shell wastes (Perna viridis) are transformed into individual calcium carbonate plate (ICCP) and apply as a support for heterogeneous catalyst. Palladium nanoparticles (3-6 nm) are deposited with even dispersion on ICCP surface as demonstrated by X-ray diffraction and scanning electron microscopy. Using the system, Sonogashira cross coupling reactions between aryl iodides and terminal acetylenes are accomplished in high yields with the use of 1% Pd/ICCP in the presence of potassium carbonate without any use of copper metal or external ligand. The Pd/ICCP can also be reused up to three times with remaining activity over 90% and negligible Pd metal leaching. This work demonstrates that mussel shell waste can be used as an inexpensive and effective support for metal catalysts in coupling reactions as demonstrated by our successful performance of Pd catalyzed, copper-free Sonogashira cross coupling process.

### Introduction

Since the discovery of Sonogashira reaction in the late 1970,<sup>[1]</sup> it became a powerful tool for construction of C(sp)-C(sp<sup>2</sup>) bond allowing the preparation of various acetylene derivatives for many research fields such as pharmaceuticals, petrochemicals and material science.<sup>[2-4]</sup> Classically, the Sonogashira reaction is catalyzed by palladium/copper catalytic complexes in the presence of phosphine ligands.<sup>[5-8]</sup> In recent years, however, copper-free Sonogashira coupling reaction has been developed in order to suppress the formation side product, diacetylenes.<sup>[9-13]</sup> <sup>[14]</sup>Even though those reaction conditions demonstrated high reactivity and specificity, the use of homogeneous catalyst system frequently causes a loss of palladium metal catalyst. Moreover, trace metal contamination in the final product and environment is very difficult to remove raising safety concern.

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Despite the use of homogeneous catalyst, heterogeneous version gains more popularity in recent year due to the ease of recyclability after use and compatibility with continuous flow systems.<sup>[15]</sup> Therefore, a number of research have been focused on the development of the solid support for palladium to catalyze Sonogashira reaction including carbon sources (e.g. graphene, charcoal<sup>[16-18]</sup> and carbon nanotube),<sup>[19]</sup> metal oxides,<sup>[20]</sup> modified silica,<sup>[21]</sup> chitosan,<sup>[22]</sup> dendrimer,<sup>[23]</sup> MOF<sup>[24]</sup> and polymers.<sup>[25-26]</sup> However, those catalysts in some cases require multi-step preparation in hash condition; suffer from high metal leaching and low reactivity requiring the use of external ligand and copper. Among supported material, calcium carbonate, an inexpensive and safe material, is widely used to embed palladium for hydrogenation so called "Lindlar catalyst" but rarely use for the Pd catalyzed C-C bond formation<sup>[27-28]</sup> especially in Sonogashira cross coupling reaction. This may be due to low reusability caused by low binding between calcium carbonate and palladium species.

Nowadays, sustainability concept has become one of the important criteria for the design of chemical process<sup>[29]</sup> bringing waste-derived materials come to attention. One of the popular example is the use of a nature-made composite materials so called biominerals as an alternative raw material for chemical industry.<sup>[30-31]</sup> Among them, calcium carbonate is the one of the most abundant in nature found in numerous marine organisms. In Asia pacific, green mussel is a common food which is harvested in aquaculture facilities. Over 100,000 tons of waste shells are produced each year.<sup>[32]</sup> Most of shell wastes were disposed as a landfill creating environmental problem. Therefore, transformation of waste shell into more high-value material would benefit not only economic but also environmental aspect. There were several reports on the use of wasted mussel shells as raw material for high value application.[33-35] Unlike precipitate calcium carbonate which is a calcite polymorphism, the calcium carbonate derived from natural shells is an aragonite polymorph which has higher biocompatibility, density and hardness which make it a suitable material in plastic, paper, glass, fiber and other industry. As for the catalytic support, a simple grounded shell particle (SP) were used in C-C bond formation to support Cu and Pd in Heck,[36] Ulman<sup>[37]</sup> and click reaction<sup>[38]</sup> with good recycling ability. Such property is attributed to the chelation of surface chitin and protein molecules to metal species. Although there are much economic and environmental benefits, an inconsistent and large size of shell particle might affect the reproducibility and performance of catalyst resulting in unequal effectiveness among each batch.<sup>17</sup>

Therefore, in this work we will prepare a new Pd supported material based on Asian green mussel shell wastes (Scheme 1) that is unlike any of the existing commercial  $Pd/CaCO_3$  or Pd loaded on simple grounded shell particle Pd/SP. The virgin shell

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waste will be converted into the individual calcium carbonate plate (ICCP) under convenient and benign process, offering a single layer calcium carbonate plates with a uniform size, smooth surface and high surface area as supported material for palladium nanoparticle. Such heterogeneous catalyst will be first used in ligand free, amine and copper free condition in Sonogashira coupling reaction to prepare diarylacetylene derivatives. The new catalyst is not only highlighted by comparisons of physical data (e.g., TEM, SEM, TGA, DLS and XRD) with Pd/SP derived simple shell particle and commercial Pd/CaCO<sub>3</sub>, but also by direct sideby-side experiments in catalyzed Sonogashira couplings. This new waste-derived heterogeneous catalyst could improve the overall energy and atom-efficiency of existing Sonogashira coupling reaction.



Scheme 1. Schematic illustration of the preparation of conventional Pd/shell particles (SP) and our Pd/ individual calcium carbonate plate (ICCP)

### **Results and Discussion**

Preparation of individual calcium carbonate plates and shell particles supported palladium (Pd/ICCP and Pd/SP) catalysts. An Asian green mussel shell is composed of thin aragonite calcium carbonate layers bound by thin organic binding layers.<sup>[39-42]</sup> To gain the advantage from this natural nanostructure, we therefore hypothesized that the wasted shell can be fragmented into a single aragonite plate so called "individual calcium carbonate plate" (ICCP) without destroying the aragonite structure. To selectively removing the organic protein binder between nacreous layers, a dry shell was sonicated in aqueous 30% H<sub>2</sub>O<sub>2</sub> for 24 hour followed by filtration with 200 mesh filter affording the ICCP. For comparison, simple grounded shell particles (SP) were prepared based on the procedure reported by Zeng<sup>[37]</sup> via physical grounding of dry shell powder which is subsequently filtered. Both Pd/ICCP and Pd/SP catalysts were prepared by deposition-reduction of disodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>) on ICCP and SP, respectively, followed by reduction with NaBH<sub>4</sub> in aqueous solution.

### Characterization of Pd/ICCP and Pd/SP

To gain more information on the structure of Pd/ICCP and Pd/SP catalyst, the SEM and EDX were measured. The SEM image shows the catalyst received from treatment of dry shell with  $H_2O_2$  under sonication yield mostly individual polygonal shaped particle with 3 micrometer size (figure 2 (bottom)). It suggests that our

process could effectively break the nacreous structure into individual calcium carbonate plate (ICCP). On the other hand, the simple grounded shell particle (SP) displays the connection among aragonite plates (figure 1a (top)). Assuming that, such process lead to the partially cracking of the nacre structure providing multiple size of shell particle which can be seen up to 9 diameter micrometer size. Moreover, palladium mapping information from energy-dispersive X-ray reveals that Pd is well dispersed onto the ICCP and SP as shown in figures 1b bottom and top, respectively. The resemble images of SEM/EDX from Pd/SP and Pd/ICCP are perhaps caused by its nanosize nature that is hardly seen in the SEM technique. To verify thickness and roughness of ICCP and SP, surface topologies of their stacked aragonite layers were attempted (figure 1c). The enlarged SEM images in figure 1d show the thickness of nacreous layer as ca. 0.4 micrometers. It clearly showed that the several nacreous layers remain intact in Pd/SP (figure 1d (top). However, the Pd/ICCP demonstrated a single particle of aragonite building block (figure 1d (bottom). It suggested that our protocol is undoubtedly selective removing the protein binder to create the highly uniform "individual calcium carbonate plates" (ICCP) which still maintain its original aragonite form. Moreover, in the edge area of Pd/ICCP, bright field transmission electron microscopy (TEM imaging shows a uniform morphology of Pd nanoparticles. The palladium nanoparticles were predominantly 5 to 8 nm in diameter with round-shape, as deduced from TEM image.

#### The X-ray diffraction (XRD) Studies.

In order to characterize the crystallinity patterns of prepared Pd catalysts (Pd/ICCP and Pd/SP) and commercial Pd/CaCO<sub>3</sub>,

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Pd/SP



с

Figure 1. (a, b, c, d) SEM and EDX image of and shell particles (top, Pd/SP) and individual calcium carbonate plates supported palladium (bottom, Pd/ICCP) catalysts.





XRD analysis was performed for all samples. The diffractograms in Figure 3 indicates different patterns among commercial CaCO3 vs. ICCP and SP suggesting the calcite and aragonite polymorphs, respectively.<sup>[43]</sup> The resemble patterns are found in before and after palladium loading of all supported materials (commercial CaCO<sub>3</sub>, ICCP and SP, Figure S23) suggesting that the Pd species is well dispersed on the surface and their particle sizes are below the XRD detection limit.





Figure 3. X-ray diffraction patterns of the Pd/CaCO3, Pd/ICCP and Pd/SP catalysts.

#### Thermogravimetric analysis

Figure 4 shows TG curves of Pd/ICCP (red line), Pd/SP (green line) and Pd/CaCO<sub>3</sub> (blue line). The TG curve obtained from industrial calcium carbonate (Figure 4, blue line) showed a thermal stability up to 600 °C with a single weight loss. This is caused by the release of carbon dioxide, given rise to the formation of calcium oxide which is in good agreement with the known literature.<sup>[44]</sup> The TG curve of Pd catalysts derived from shell calcium carbonate (Pd/ICCP, Pd/SP) on the other hands, displays two major weight losses. The new decomposition is founded at 200-300 °C while the second one which is similar to Pd/CaCO3 is at 600-800 °C. The new mass lost are corresponded to volatile organic content such as protein and chitin from shell. Interestingly, mass lost in the cast of Pd/ICCP, Pd/SP are detected at 2.5 and 5.5 % respectively. These results confirmed that our preparation method for ICCP partially remove organic binder that was holding nacreous layers together but the organic matrices on the surface which binds more strongly to the aragonite plate were still preserved. This organic matrix has to be maintained in order to stabilize Pd nanoparticle and increase the reusability of catalyst in contrast to bare commercial Pd/CaCO<sub>3</sub>.

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Figure 4. Thermal gravimetric (TG) thermogram of Pd/ICCP, Pd/SP and Pd/CaCO\_3  $\,$ 

#### IR spectroscopic studies

In FTIR analysis, we found that the peak at 1443.7 and 1444.4 cm<sup>-1</sup> of ICCP and SP support, confirming the characteristic stretching vibrations of C-O in aragonite form (Figure S24). On the other hands, the structure of commercial CaCO<sub>3</sub> was corresponded to calcite morphology as the observation of characteristic absorption peak at lower wavenumber at 1389.2 cm<sup>-1</sup>. The deposition of palladium into commercial CaCO<sub>3</sub> resulted in an insignificant shift by 1.5 cm<sup>-1</sup>. In case of waste shell derived catalysts Pd/ICCP and Pd/SP, up to 5 cm<sup>-1</sup> shift were observed suggesting stronger interaction between  $CO_3^{2-}$  from waste shell and Pd species in comparison with commercial CaCO<sub>3</sub>. The reason for the stronger interaction between calcium carbonate in aragonite form in comparison with calcite is still unclear and need to be further clarified.

#### Determination of Palladium content by ICP-OES analysis

Before the examination of catalytic activity of prepared catalyst, Pd/ICCP, Pd/SP, Pd/CaCO3 and Pd/C contents were first determined using inductively coupled plasma optical emission spectrometry analysis (ICP-OES analysis) (table 1). Pd content in those heterogeneous catalysts derived from the waste shell, Pd/ICCP, Pd/SP were found at 6.6 and 5.7% (wt./wt.) respectively (Table 1, entry 1 and 2). The higher loading of Pd/ICCP over Pd/SP is perhaps due the surface morphology of the support. To gain more information on the suface area of the support, BET analysis of both supports were performed. Specific surface ares of ICCP (6.12 m<sup>2</sup>g<sup>-1</sup>) is slightly higher than SP (4.21 m<sup>2</sup>g<sup>-1</sup>) which supports the result of Pd loading in ICCP and SP. Also, we hypothesized that the stacked nacreous in SP gave roughness surface causing the reduction of the binding efficiency of Pd nanoparticle toward the SP support. On the other hands, the smoothness of ICCP surface facilitates the embedding between Pd nanoparticle and ICCP. For comparison reason, the commercial 5%Pd/CaCO3 and 10%Pd/C were analyzed under the same method as above mentioned (Table 1, entry 3 and 4). The slightly loss of Pd amount in those catalysts were observed which is probably due to the decomposition under bench storage. The palladium level measured here will be used for the entire experiments in this investigation.

analysis <sup>a</sup>			
Entry	Catalyst	Expected Pd Content	Pd Content <sup>a</sup>
1	Pd/ICCP	7.0	6.1 ± 0.1%
2	Pd/SP	7.0	5.7 ± 0.1%
3	Pd/CaCO <sub>3</sub>	5.0	4.3 ± 0.1%
4	Pd/C	10.0	6.9 ± 0.3%

Table 1 Determination of Palladium content in the catalysts from ICP-OES

<sup>a</sup> Palladium weight percentage was determined from ICP-OES analysis.

### **Reaction condition screening**

With the catalysts in hand, we began our optimization of Sonogasira coupling reaction between 4-iodotoluene (1b) and phenyleneethynylene (2a) without copper and ligand (Table 2). Using the known procedure,<sup>[45]</sup> the use of 1 % of Pd/C with ethanol as solvent and potassium carbonate gave a full conversion of starting iodide and provide the product 3b in 86%yield (table 2, entry 1). Switching from the Pd/C into commercial Pd/CaCO<sub>3</sub>, the coupling product was obtained in excellent yield with no remaining starting material detected by GC (table 2, entry 2). To the best of our knowledge, this is the first use of Pd/CaCO<sub>3</sub> as heterogeneous catalyst for Sonogasira coupling reaction. Next, the wasted shell derived catalyst Pd/SP and Pd/ICCP were subjected to above condition. When Pd/SP was used as a catalyst, an incomplete reaction was observed and produced only 75% of coupling product 3b with the remaining starting material. On the other hand, no starting remains in the reaction condition in case of Pd/ICCP and 94% of target product 3b was received. The efficiency of Pd/ICCP over Pd/SP is perhaps governed by the high surface are of ICCP support. We would like to note here that this reaction condition is environmentally friendly and cost effective. Ethanol and K2CO3 are the safe and inexpensive chemicals favoring to use in the industry according to EPA guideline.<sup>[46]</sup> Importantly, there is no need to use copper and extra ligand in the reaction condition. We also ensured that there is no trace cooper in our reaction by repeating the reaction using the new glassware and freshly distilled solvent. Moreover, trace analysis of copper performed by ICP-OES in Pd/ICCP and all reagents used in the reaction confirmed that no copper were present within the detection limit. Even though, we are satisfied with the reaction condition but the effect of solvent and base were further investigated to see their generality. Switching base from K<sub>2</sub>CO<sub>3</sub> to DIPA and Cs<sub>2</sub>CO<sub>3</sub> or solvent from EtOH to MeCN and DMSO, resulted in dramatically poor yields. The perforation of this reaction condition comes from basicity and solubility of base and solvent used in the reaction condition.

3a-

92 % 3c

71 % 3i

64 %

65 %

90 % 3r

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<sup>a</sup>Reaction condition: 4-iodotoluene (0.5 mmol), phenyl acetylene (0.6 mmol) catalysts (0.005 mmol), bases (1.0 mmol), in solvents (6.0 mL). <sup>b</sup>Determined from the GC measurement.

#### Substrate Scope

To evaluate substrate scope of this method, variety functional groups need to be tested. Therefore, a series of aryl iodides either commercially available or prepared according to literature procedures were subjected to the coupling reaction with phenyl acetylene in the presence of 2 mol % of Pd/ICCP under the optimized reaction conditions (Table 1, entry 12) and the results were summarized in Table 3. Good to excellent yields were generally obtained after the column chromatography. The aryl iodides bearing an electron donating group, such as methyl, naphthyl, biphenyl and, methoxy (1a-1g) yielded the desired bisarylacetylenes in excellent yields (3a-3g). However, the cross-coupling of aryl iodides (1e) gave a fair yield of the target product 3e under the optimized condition suggesting the steric effect of the reaction. Aryl iodide bearing electron-withdrawing groups for example, nitro, keto, aldehyde, cyano and trifluoromethyl moieties were smoothly reacted with phenylacetylene to generate the the diarylacetylene in good yields (3i-3m). Nitrogen containing substrate such as 4-iodo aniline (1n), phenylazide (1o) and pyridine (1p) were also suitable for this transformation as they afforded the target compounds (3n-p) in good yields. Moreover, other leaving groups, such as chloro (1q) and bromo (1r) groups were well tolerated under reaction conditions and were reacted selectively, giving the desired products in good to excellent yields(3q-r).



<sup>a</sup>Reaction condition: aryl iodides (0.5 mmol), phenyl acetylene (0.6 mmol) Pd/ICCP (0.005 mmol), potassium carbonate (1.0 mmol), in EtOH (6.0 mL), solution at 100 °C. blsolated yields.

6.1% Pd/ICCP [1 mol%]

100 °C, EtOH, K<sub>2</sub>CO<sub>3</sub>, 4 h

84 % 3b

57 %

88 % 3h

quant. 3k

85 % 3n

89 %

3q

2a

88 %

90 % 3d

80 % 3a

91 % 3i

74 % 3m

86 %

3p

We also expand the scope of the reaction into various terminal alkyne substrates. The representative phenyl acetylenes bearing electron-withdrawing (2b) and electron-donating groups (2c) were proceeded smoothly under optimized reaction condition with iodobenzene (1b) providing the coupled products 3s and 3t in excellent yields. Moreover, terminal alkyne having alkyl substituent such as 2d, were reacted with 1b to generate the desired product 3u in good yield.



Scheme 2 Substrate scope of terminal alkynes in the reaction with iodobenzenes

#### **Reusability and metal leaching studies**

To determine the reusability of catalyst, the three consecutive runs of each catalyst including Pd/ICCP, Pd/SP and Pd/CaCO<sub>3</sub> were performed and the %conversion were carefully monitored by GC. Table 4, we would like to note here that the catalyst reuse process involves only filtration of the reaction solution, wash with EtOH/water and drying in vacuum without any activation via chemical or high temperature treatment. Significant

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losses of activity were found in both Pd/SP and Pd/CaCO<sub>3</sub> since second cycle. However, the Sonogashira reaction using Pd/ICCP for three cycles gave the excellent conversion between 100-90%. Significant losses of catalyst activity were found in both Pd/SP and Pd/CaCO<sub>3</sub> which may result from the catalyst deactivation and leaching. The roughness surface of stacked aragonite in SP may cause metal leaching due to the poor interaction between Pd species and support. On the other hands, unlike the flat aragonite in ICCP, commercial CaCO<sub>3</sub> are found in form of calcite, therefore the pore in those supports might be clogged during byproduct generation in the reaction which cannot be washed away before the next cycle. Also, lack of protein biding on the surface of commercial CaCO<sub>3</sub> could result in the loss of Pd species in each cycle. To prove the hypothesis, metal leaching of each catalyst was quantified. The reaction mixtures after the first run were filtered and the crude products were subjected to ICP analysis. Palladium contents in crude products from Pd/ICCP, Pd/SP and Pd/CaCO<sub>3</sub> were founded as followed 1.1, 1.4 and 8% wt./wt. The result confirms the significant loss of Pd content in Pd/CaCO3 catalyst. On the other hands, negligible leaching of Pd contents from the catalyst supported on waste shell in either SP or ICCP are perhaps due to the strong chelation between Pd and protein on the surface of the shell supports. Therefore, Pd/ICCP catalyst is a promising option for low level leaching metal heterogeneous catalyst with high reactivity and reusability.



<sup>a</sup>Reaction condition: 4-iodotoluene (0.5 mmol), phenyl acetylene (0.6 mmol) catalysts (0.005 mmol), bases (1.0 mmol), in solvents (6.0 mL). <sup>b</sup>Determined from the GC measurement. <sup>c</sup>Determined by ICP-OES from crude after 1<sup>st</sup> run.

### Conclusions

In summary, we have developed a new heterogeneous palladium catalyst supported on individual calcium carbonate plate (ICCP) derived from waste Asian green mussel shell. The catalyst has been shown to be highly active for copper and ligand free Sonogashira coupling reaction. The reaction proceeds in excellent yield with a variety of aryl iodides and terminal alkynes. The Pd/ICCP also exhibits reusability while the simple Pd/SP and Pd/CaCO<sub>3</sub> cannot be reused. As it is convenient to be prepared from shell waste and demonstrates high and stable activity;

Pd/ICCP should serve as a catalyst of choice for green Sonogashira coupling reactions.

### **Experimental Section**

#### Materials and methods

All reagents were purchased from Sigma-Aldrich, Fluka® (Switzerland) or Merck® (Germany) and used without further purification. Analytical thinlayer chromatography (TLC) was performed on Kieselgel F-254 pre-coated plastic TLC plates from EM Science. Gel column chromatography was carried out with silica gel (60, 230-400 mesh) from ICN Silitech. The <sup>1</sup>Hand <sup>13</sup>C-NMR spectra were obtained on a Varian Mercury NMR spectrometer, which operated at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C nuclei (Varian Company, CA, USA) The morphological structure of ICCP and SP was observed using a scanning electron microscope (SEM, JEOL JSM-6510A) operating at 20 kV under a high vacuum mode with a secondary electron image (SEI) detector. The elemental composition analysis of the material was investigated using a built-in energy dispersive X-ray spectrometer (EDS). The morphological structure of Pd nanoparticles on individual calcium carbonate plate was observed using a transmission electron microscopy (TEM, JEOL, JEM-2100) operating at 100-120 kV. The XRD patterns were recorded by an X-ray diffractometer (DMAX 2200 Rigaku) under Cu Ka radiation. All ATR FT-IR spectra were recorded using a germanium micro-IRE with Nicolet 6700 FT-IR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector at 4 cm<sup>-1</sup> resolution and 128 co-addition scans. Surface area analyzer, N2 adsorption-desorption isotherms and BET specific surface area of the catalysts were carried out using a BEL Japan, BELSORP-mini instrument.

#### Preparation of tetrachloropalladic acid $(H_2PdCl_4)$ solution

A mixture of palladium metal (1g) in aqua regia (5 mL, a mixture of concentrated nitric acid and hydrochloric acid with a ratio of 3:1 v/v) was stirred at 100 °C until palladium was completely dissolved. The solution was then kept heating until almost dry and pouring into a 100-mL volumetric flask. Water was added to adjust concentration of H<sub>2</sub>PdCl<sub>4</sub> to 0.094 M.

# Preparation of the individual calcium carbonate plates and shell particles supported palladium (Pd/ICCP and Pd/SP) catalysts

Asian green mussel (Perna viridis) shells were first cleaned to remove residual tissues and other contaminants then drving under an ambient air. The dried shells were baked at 200 °C for 2 h. The thermal-treated shells were submerged in 30 % (wt./wt.) hydrogen peroxide solution under ultrasonic sonication for 24 h to dissolve the degraded organic binder. The treated-shells were filtered with 200 mesh filter size to obtain individual calcium carbonate plates. After that, the individual calcium carbonate plates were washed with water several times and air dried before keeping in a desiccator for preparation of individual calcium carbonate plates supported palladium (Pd/ICCP) catalyst. A solution of 0.094 M H<sub>2</sub>PdCl<sub>4</sub>25 mL was rapidly added into 5 grams of the individual calcium carbonate plates in 100 mL water. The mixture was stirred until color changed from yellow to colorless. The powders washed with water until the color of supernatant turned colorless. Finally, the catalyst was reduced with 1.2 equivalent of sodium borohydride for 1 h. Shell particles supported palladium (Pd/SP) catalyst was prepared by the same procedure but grounded shell particles, without hydrogen peroxide treatment, was used instead.

General procedure for Sonogashira coupling reaction

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A sealed tube equipped with a magnetic stirring bar was charged with  $K_2CO_3$  (1.0 mmol) and Pd catalyst (1 mol%). Aryl iodide (0.5 mmol), terminal alkyne (0.6 mmol), and ethanol (6 mL) were added. Stirring was continued at 100 °C under nitrogen for 4 hour, and then cooled to room temperature. The reaction mixture was filtered. The residue was purified by chromatography, eluting with hexane and ethyl acetate.

1,2-diphenylethyne (3a).<sup>[26]</sup> [CAS: 501-65-5]:)

According to the general procedure, the reaction was performed by using 4-iodobenzene (102 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford 3a (78.4 mg, 0.44 mmol, 88%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (dd, *J* = 6.6, 1.8 Hz, 4H), 7.51 – 7.32 (m, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  131.67, 128.40, 128.30, 123.37, 89.47; GC-MS: m/z: 178.1.

1-methyl-4-(phenylethynyl)benzene<sup>[26]</sup> (3b). [CAS: 3287-02-3]:

Synthesized according to procedure A using 4-iodotoluene (109 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3b** (80.7 mg, 0.42 mmol, 84%) as a colorless solid. <sup>1</sup>H NMR (400 MHz, CDCI3)  $\delta$  7.57 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.31 (m, 3H), 7.20 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCI3)  $\delta$  138.39, 131.57, 131.53, 129.13, 128.33, 128.08, 123.54, 120.26, 89.60, 88.76, 21.50; GC-MS: m/z: 192.0.

1-methyl-3-(phenylethynyl)benzene<sup>[26]</sup> (3c). [CAS: 14635-91-7]:

Synthesized according to procedure A using 3-iodotoluene (109 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3c** (88.4 mg, 0.42 mmol, 92%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.53 (m, 2H), 7.40 (dd, *J* = 11.3, 5.2 Hz, 5H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.46, 132.65, 132.06, 129.61, 129.15, 128.78, 128.69, 128.61, 123.88, 123.57, 90.05, 89.51, 21.66; GC-MS: m/z: 191.9.

1-methyl-2-(phenylethynyl)benzene<sup>[26]</sup> (3d). [CAS: 14309-60-5]:

Synthesized according to procedure A using 2-iodotoluene (109 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3d** (86.5 mg, 0.45 mmol, 90%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.53 (m, 2H), 7.40 (dd, *J* = 11.3, 5.2 Hz, 5H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.46, 132.65, 132.06, 129.61, 129.15, 128.78, 128.69, 128.61, 123.88, 123.57, 90.05, 89.51, 21.66; GC-MS: m/z: 191.9.

2-iodo-1,3-dimethylbenzene (3e)<sup>[47]</sup>. [CAS: 180783-48-6]:

Synthesized according to procedure A using 2-iodo-1,3-dimethylbenzene (116 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3e** (56.7 mg, 0.28 mmol, 55%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\overline{0.46}$  7.57 (m, 2H), 7.47 – 7.33 (m, 3H), 7.18 (dt, *J* = 19.5, 6.9 Hz, 3H), 2.60 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\overline{0.4038}$ , 131.52, 128.48, 128.20, 127.90, 126.83, 124.01, 123.13, 98.00, 87.30, 21.22.; GC-MS: m/z, 205.9.

1-methoxy-4-(phenylethynyl)benzene<sup>[26]</sup> (3f). [CAS: 7380-78-1]:

Synthesized according to procedure A using 1-iodo-4-methoxybenzene (117 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3f** (91.6 mg, 0.44 mmol, 88%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.95 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 7.2 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.42 – 7.34 (m, 3H), 2.61 (d, J = 6.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl3)  $\delta$  197.22, 136.24, 131.76, 131.70, 128.82, 128.46, 128.27, 128.20, 122.70, 92.75, 88.66, 26.55; GC-MS: m/z: 207.9.

4-(phenylethynyl)aniline<sup>[48]</sup> (3g). [CAS: 1849-25-8]:

Synthesized according to procedure A using 4-iodoaniline (110 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford 3g (82.1 mg, 0.43 mmol, 85%) as a brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 – 7.37 (m, 2H), 7.30 – 7.19 (m, 5H), 6.55 (d, J = 8.4 Hz, 2H), 3.72 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.79, 133.09, 131.49, 128.39, 127.78, 114.89, 114.75, 112.79, 90.26, 87.47; GC-MS: m/z: 218.9.

1-chloro-4-(phenylethynyl)benzene<sup>[49]</sup> (3h). [CAS: 5172-02-1]:

Synthesized according to procedure A using 1-chloro-4-iodobenzene (119 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford 3h (94.6 mg, 0.44 mmol, 89%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.62 – 7.54 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.32 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl3)  $\delta$  134.39, 132.93, 131.73, 128.81, 128.59, 128.51, 123.10, 121.95, 90.49, 88.40; GC-MS: m/z: 211.8.

1-bromo-4-(phenylethynyl)benzene<sup>[50]</sup> (3i). [CAS: 13667-12-4]:

Synthesized according to procedure A using 1-bromo-4-iodobenzene (141 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford 3i (115.7 mg, 0.44 mmol, 90%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 – 7.45 (m, 4H), 7.43 – 7.31 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.17, 131.76, 131.74, 128.65, 128.54, 123.08, 122.62, 122.42, 90.66, 88.45; GC-MS: m/z: 255.8.

1-nitro-4-(phenylethynyl)benzene<sup>[51]</sup> (**3j**). [CAS: 1942-30-9]:

Synthesized according to procedure A using 1-iodo-4-nitrobenzene (125 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3j** (101.6 mg, 0.44 mmol, 91%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  8.21 (d, *J*=8.7 Hz, 2H), 7.66 (d, *J*=8.8 Hz, 2H), 7.56 (dd, *J*=5.9, 2.6 Hz, 2H), 7.46 – 7.32 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.11, 132.37, 131.96, 130.37, 129.40, 128.66, 123.74, 122.23, 94.83, 87.68; GC-MS: m/z: 222.9.

1-(4-(phenylethynyl)phenyl)ethanone<sup>[26]</sup> (3k). [CAS: 1942-31-0]:

Synthesized according to procedure A using 1-(4-iodophenyl)ethanone (123 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3k** (112.2 mg, 0.51 mmol, 102%(quantitative yield)) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.42 – 7.34 (m, 3H), 2.61 (d, *J* = 6.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  197.22, 136.24, 131.76, 131.70, 128.82, 128.46, 128.27, 128.20, 122.70, 92.75, 88.66, 26.55; GC-MS: m/z: 219.9.

4-(phenylethynyl)benzaldehyde<sup>[52]</sup> (31). [CAS: 57341-98-7]:

Synthesized according to procedure A using 4-iodobenzaldehyde (116 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005  $\,$ 

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mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3I** (65.9 mg, 0.32 mmol, 64%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.02 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.43 – 7.32 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  191.50, 135.57, 132.24, 131.93, 129.70, 129.10, 128.61, 122.65, 93.59, 88.66.; GC-MS: m/z: 205.9.

1-(phenylethynyl)-4-(trifluoromethyl)benzene<sup>[26]</sup> (3m). [CAS: 370-99-0]:

4-(phenylethynyl)benzonitrile<sup>[53]</sup> (3n). [CAS: 29822-79-5]:

Synthesized according to procedure A using 4-iodobenzonitrile (114 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford 3n (72.2 mg, 0.35 mmol, 71%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.64 (q, *J* = 8.3 Hz, 4H), 7.60 – 7.53 (m, 2H), 7.47 – 7.34 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  132.08, 132.04, 131.80, 129.14, 128.52, 128.26, 122.26, 118.50, 111.51, 93.81, 87.75; GC-MS: m/z: 202.9.

1-azido-4-(phenylethynyl)benzene<sup>[54]</sup> (30). [CAS: 669090-70-4]:

Synthesized according to procedure A using 1-azido-4-iodobenzene (122 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford 30 (71.2 mg, 0.32 mmol, 65%) as a brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (q, *J* = 8.3 Hz, 4H), 7.60 – 7.53 (m, 2H), 7.47 – 7.34 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  132.08, 132.04, 131.80, 129.14, 128.52, 128.26, 122.26, 118.50, 111.51, 93.81, 87.75; GC-MS: m/z: 219.1.

1-(phenylethynyl)naphthalene<sup>[26]</sup> (**3p**). [CAS: 4044-57-9]:

Synthesized according to procedure A using 1-iodonaphthalene (127 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3p** (93.6 mg, 0.41 mmol, 82%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.56 (d, *J* = 8.3 Hz, 1H), 7.88 (dt, *J* = 21.1, 11.4 Hz, 3H), 7.80 – 7.65 (m, 3H), 7.60 (dd, *J* = 14.3, 7.2 Hz, 1H), 7.56 – 7.37 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.75, 133.69, 132.12, 130.82, 129.21, 128.88, 128.82, 128.76, 127.22, 126.87, 126.68, 125.72, 123.89, 121.38, 94.81, 88.03; GC-MS: m/z: 228.0.

4-(phenylethynyl)-1,1'-biphenyl<sup>[55]</sup> (3q). [CAS: 15784-39-1]:

Synthesized according to procedure A using 4-iodo-1,1'-biphenyl (140 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3q** (101.7 mg, 0.40 mmol, 80%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (dt, *J* = 8.1, 5.9 Hz, 8H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.35 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.43, 140.82, 132.49, 132.08, 129.31, 128.82, 128.72, 128.08, 127.47, 123.78, 122.66, 90.55, 89.79; GC-MS: m/z: 253.9.

3-(phenylethynyl)pyridine<sup>[56]</sup> (3r). [CAS: 13238-38-5]:

Synthesized according to procedure A using 3-iodopyridine (103 mg, 0.5 mmol), ethynylbenzene (51 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol),

potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3r** (179.2 mg, 0.43 mmol, 86%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\bar{o}$  8.77 (d, J = 1.4 Hz, 1H), 8.55 (dd, J = 4.9, 1.6 Hz, 1H), 7.82 (dt, J = 7.9, 1.9 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.42 – 7.33 (m, 3H), 7.29 (ddd, J = 7.8, 4.9, 0.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\bar{o}$  152.25, 148.52, 138.70, 131.85, 128.98, 128.60, 123.22, 122.66, 120.73, 92.91, 86.00; GC-MS: m/z: 178.9.

1-fluoro-4-(phenylethynyl)benzene<sup>[57]</sup> (3s). [CAS: 405-29-8]:

Synthesized according to procedure A using 4-iodobenzene (102 mg, 0.5 mmol), 1-ethynyl-4-fluorobenzene (72 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3s** (81.4 mg, 0.42 mmol, 83%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.52 (dt, *J* = 9.1, 5.2 Hz, 4H), 7.35 (dd, *J* = 9.2, 4.8 Hz, 3H), 7.04 (t, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.89, 161.41, 133.65, 133.57, 131.70, 128.50, 128.46, 123.27, 119.56, 119.53, 115.87, 115.65, 89.20, 88.45; GC-MS: m/z: 195.9.

1-methoxy-4-(phenylethynyl)benzene<sup>[26]</sup> (3t). [CAS: 7380-78-1]:

Synthesized according to procedure A using 4-iodobenzene (102 mg, 0.5 mmol), 1-ethynyl-4-methoxybenzene (79 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford 3t (84.3 mg, 0.41 mmol, 81%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.43 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.16 (m, 3H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.71 (s, 3H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.77, 133.17, 131.57, 128.42, 128.04, 123.75, 115.53, 114.14, 89.53, 88.21, 55.37; GC-MS: m/z: 207.9.

oct-1-yn-1-ylbenzene<sup>[58]</sup> (3u). [CAS: 16967-02-5]:

Synthesized according to procedure A using 4-iodobenzene (102 mg, 0.5 mmol), oct-1-yne (66 mg, 0.6 mmol), Pd/ICCP (9 mg, 0.005 mmol), potassium carbonate (138 mg, 1.0 mmol) in EtOH (6 mL) for 4 h to afford **3u** (73.6 mg, 0.40 mmol, 79%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (dd, J=7.5, 2.0 Hz, 2H), 7.35 – 7.25 (m, 3H), 2.44 (t, J=7.1 Hz, 2H), 1.67 – 1.62 (m, 2H), 1.55 – 1.32 (m, 10H), 0.94 (d, J=6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  131.99, 128.60, 127.86, 90.91, 81.04, 31.83, 29.21, 29.06, 23.01, 19.87, 14.48.; GC-MS: m/z: 186.0.

#### General procedure for reuse of heterogeneous palladium catalysts

The heterogeneous palladium catalyst was separated from the reaction mixture by filtration. The reused palladium catalyst was washed with ethanol, followed by removal of the solvent under a reduced pressure before the next reaction.

# General procedure for scanning electron microscopy and energy dispersive X-ray (SEM and EDX) analysis

Scanning electron microscope (SEM, JEOL, JSM-6510A) was employed for the structural investigation of morphology of the individual calcium carbonate plates and shell particles supported palladium (Pd/ICCP and Pd/SP) catalysts under a low acceleration voltage of 5 kV. To collect SEM images, a specimen was wrapped with an aluminum foil before mounting onto a modified stub with the cross-sectioned surface normal to the electron beam. The elemental composition analysis of the materials was investigated using a built-in energy dispersive X-ray spectrometer (EDS).

#### Determination of organic content

The organic contents in the Pd/ICCP and Pd/SP catalysts were quantitatively determined by thermal gravimetric analysis (PerkinElmer, Pyris 1). The catalyst was loaded into a ceramic crucible and heated up to 850 °C at a heating rate of 20 °C/min under nitrogen environment.

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[26] General procedure for transmission electron microscopy (TEM) 1069-1064 analysis

Transmission electron microscopy (TEM, JEOL, JEM-2100) was employed for the structural investigation of morphology of the individual calcium carbonate plates supported palladium (Pd/ICCP), operated at 100-120 kV. To collect TEM images, a particle was dropped onto grids for transmission electron microscopy.

#### General procedure for surface area analysis

The sample weights were nearly 40.0 mg and weighted exactly after pretreatment at 200 °C for 2 hr. Glass rods were placed at sample cell and blank cell positions after that the samples were analyzed with BEL-sorpmini instrument.

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