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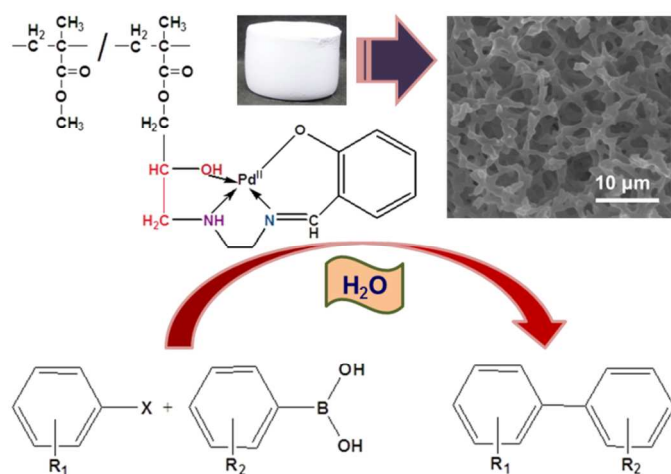
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Mahasweta Nandi and Hiroshi Uyama

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Porous Acrylate Monolith Supported Pd Nanoparticles: Highly Active and Reusable Catalyst for Suzuki-Miyaura Reaction in Water

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Abstract

The present work describes the use of Palladium-Schiff-base functionalized methyl methacrylate-glycidyl methacrylate (MMA-GMA) copolymer monoliths for SMC reaction of aryl halides in water under aerobic conditions. Highly porous MMA-GMA copolymer monoliths with interconnected network morphology have been fabricated by thermally induced phase separation technique (TIPS). The copolymer synthesized here *via* radical polymerization has a molecular weight of 162000 and GMA content of 11 mole%. The monoliths have been functionalized by aminolysis of the epoxy groups by ethylene diamine, followed by their condensation with salicylaldehyde to form the Schiff base. The donor atoms of the Schiff base bind Pd(II) ions very efficiently to generate an ortho-metallated Pd(II)-Schiff base complex anchored on acrylate copolymer monoliths (**Pd-SBAM**). The material has been found to exhibit excellent catalytic activity, high stability and turn over frequency (TOF) for SMC reactions. The biphenyl products have been obtained with very high yield and the catalyst could be reused for several reaction cycles without significant loss in its activity. Moreover, the heterogeneous catalyst has been developed in the form of a monolith, which facilitates its easy separation from the reaction medium.

Introduction

Palladium catalyzed Suzuki-Miyaura cross-coupling (SMC) reaction for the formation of C–C bond is an important synthetic tool in modern organic chemistry¹⁻⁴ and an area of major research interest.⁵⁻¹¹ Different catalytic systems for SMC reactions have been reported; most of them being homogeneous and use soluble palladium complexes in an organic solvent or in a mixture of water and an organic solvent. Over the years, though the catalytic activity could be improved significantly, large scale industrial application of the catalysts remains challenging as they are expensive and cannot be separated from the reaction media efficiently. Thus heterogeneous Pd-catalysts which offer high activity and selectivity in the cross-coupling reactions are highly desirable to overcome some of these disadvantages. Thus, in recent years, much effort has been given to design safe, effective and recyclable heterogeneous catalysts. There are several reports of Pd-nanocatalyst immobilized on solid supports, such as carbon,¹² zeolites,^{13,14} mesoporous silica,¹⁵ metal oxides,¹⁶ graphite oxide¹⁷ and polymers^{18,19} for SMC reactions. Immobilization of palladium species over a solid support *via* covalent interaction is more profitable as compared to conventional impregnation since it minimizes leaching of the active sites into the reaction mixture and improves the stability of the catalyst. For large scale industrial application easy and cheap synthetic process with high activity and durability of the catalyst are desirable. In this respect polymeric materials can be highly attractive and heterogenization of metal complexes over them can be accomplished by modification of their surface functionalities. Palladium complexes with Schiff base,^{20,21} dendrimer^{22,23} and N-heterocyclic carbene ligands^{24,25} anchored to polymer supports have been reported previously. Among these, Schiff base ligands are particularly interesting as they show good selectivity and sensitivity toward different metal ions. But their use in homogeneous catalytic systems is limited due to their tendency to form inactive dimeric peroxo- and μ -oxo species.²⁶⁻²⁸ In order to overcome this problem, anchoring the Schiff-base complex over functionalized polymer support could be a reasonable approach.

There are reports of a wide range of catalytic systems for SMC reactions, as mentioned above, but very few of them function in environmentally friendly aqueous medium. Most of the systems rely on the use of environmentally hazardous organics as solvents or high catalytic concentrations. So a catalyst which can also function in aqueous medium even at a very low concentration of palladium is highly demanding for both economic and environmental reasons.

On the other hand, heterogeneous catalysts containing nanoscale palladium particles as the active catalytic species for SMC reaction suffer from poor recyclability due to the formation of less reactive palladium black aggregates. This can be overcome by generating the active Pd(0) species *in situ* under the reaction conditions from Pd(II) under aerobic conditions which can suppress the reduction of the later and its subsequent agglomeration to Pd(0) nanoparticles.¹³

Herein we report a methyl methacrylate-glycidyl methacrylate (MMA-GMA) co-polymer monolith supported Schiff base-Pd(II) complex and its application as an efficient and recyclable heterogeneous catalyst in SMC reaction in water under aerobic conditions. The highly cross-linked MMA-GMA co-polymer monoliths are fabricated by a facile and neat thermally induced phase separation (TIPS) technique previously established by our group and subsequently modified with ethylene diamine and salicylaldehyde to generate salen type of Schiff base donor sites^{29,30} (**III**) which can efficiently bind to Pd(II) (Scheme 1) to give **Pd-SBAM** (**IV**). Monoliths have been preferred here as catalyst support due to their good mechanical strength, ease of chemical modification and large permeability which promotes fast mass transfer. Moreover, fabrication of the catalysts in the form of monolith makes their separation from the reaction medium much easier than conventional catalysts in powder form. On the other hand, acrylate resins are chosen as the copolymer for the fabrication of monolith as they are thermosetting plastic substances which can be molded conveniently and have unique characteristic properties like toughness and antiweatherability. The Pd(II) bound material, **Pd-SBAM**, thus obtained can be used as a catalyst for facile Suzuki Miyaura cross-coupling (SMC) reaction of aryl halides in water under aerobic conditions. The catalytic system used here has several advantages like it does not produce any organic solvent or metal-contaminated waste, it is stable in air and moisture and the reaction can be done under environmentally benign conditions.

Experimental Section

Materials and Physical Measurement

Methyl methacrylate (MMA), glycidyl methacrylate (GMA), azobisisobutyronitrile (AIBN) and palladium acetate (Pd(OAc)₂) have been purchased from Wako Chemicals, Japan. Ethylene diamine (*en*), salicylaldehyde and the other solvents (toluene, methanol and ethanol) used for the experiments have been procured from Nacalai Tesque, Japan. Size-exclusion chromatographic analysis has been carried out using a TOSOH SC-8020 apparatus with a

refractive index detector at 313 K under the following conditions: TOSOH TSKgel G3000H_{HR} column and chloroform eluent at a flow rate of 1.0 mL/min (Tosoh, Tokyo, Japan). The calibration curve has been obtained using polystyrene as the standard. Fourier transform infrared (FT-IR) measurements of the samples by the attenuated total reflectance (ATR) method have been performed using the Thermo Scientific (Yokohama, Japan) Nicolet iS5 spectrometer equipped with iD5 ATR attachment. A Hitachi S-3000N scanning electron microscope (SEM), Tokyo, Japan, operated at 15 kV has been used for the determination of the microstructure of the monoliths. Prior to the measurements, the monolith samples have been slivered into thin sections with a scalpel and adhered on the probe followed by their coating with a thin layer of gold using an ion sputter apparatus, E-1010 Hitachi Ltd, Tokyo, Japan. Transmission electron microscopy (TEM) images of the catalysts at different conditions have been recorded in a Hitachi H-7650 transmission electron microscope. Before observation of the TEM images, the sample grids have been prepared by dropping the ball-milled catalysts dispersed in aqueous solution onto a thin layer of amorphous carbon coated copper TEM grid (ϕ 3.0 mm, 400 mesh). X-ray photoelectron spectroscopy (XPS) studies have been carried out using a PHI, Quantera SXM, Ulvac-PHI Inc., Japan operated with monochromatic Al (1486.6 eV) as the X-ray source. Pd contents in the catalyst and in the reaction mixture have been analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a Shimadzu ICPS-7510 Sequential Plasma Emission Spectrometer. ¹H nuclear magnetic resonance (NMR) spectra have been recorded on a Bruker DPX-400 spectrometer using tetramethylsilane as the internal standard. Gas chromatographic studies have been carried out using a Shimadzu GC-2014 gas chromatograph.

Synthesis of catalyst (Pd-SBAM)

For the synthesis of the copolymer MMA-GMA, 30 g of MMA and 4.6 g of GMA are taken in a round-bottomed flask containing 80 mL of toluene. To it 0.04 g of AIBN is added as the polymerization initiator and the air inside the flask is replaced by Ar. The mixture is then stirred at 353 K for 4 h under Ar atmosphere and the resulting solution is added drop wise to a large volume of methanol. The polymer precipitated in methanol is collected by filtration, washed repeatedly with methanol and finally dried under vacuum under ambient temperature.

Monoliths of the copolymer are prepared by thermally induced phase separation (TIPS) technique. In a typical procedure, 80 mg of MMA-GMA copolymer is dissolved in 1 mL mixture

of 4/1 volume ratio of ethanol/water by heating at 333 K. Then the solution is cooled at 293 K under static condition inducing phase separation of the polymer in the form of a monolith. The monolith is recovered, washed several times with water to remove the trapped solvent molecules and subsequently dried under vacuum. For aminolysis of the epoxy groups, the monoliths are treated with a methanolic solution of ethylene diamine (2.5 times with respect to epoxide) at 323 K for 4 h. After washing and drying, the amine groups in the polymer monolith are treated with salicylaldehyde (2.0 times with respect to epoxide) in methanol for 6 h at 333 K to form Schiff-base modified MMA-GMA copolymer. Finally the catalyst, **Pd-SBAM**, is obtained by soaking the monolith in a Pd(OAc)₂ solution in toluene overnight at room temperature, followed by repeated washings with toluene. After drying, the material is ready to be used as catalyst. The general protocol for the synthesis of **Pd-SBAM** has been given in Scheme 1.

Catalysis

In a typical catalytic cycle, 1.0 mmol of the aryl halide, 1.2 mmol of aryl boronic acid and 2.5 mmol of base are taken in 10 mL of water and the mixture is preheated to 333 K. The reaction is started with the addition of 0.02 g of **Pd-SBAM** (5.536×10^{-4} mmol Pd) as the catalyst. The reactions are continued for 4-5 h and the products are extracted in diethyl ether. The solvent is evaporated by rotary evaporation followed by vacuum drying and known amount of 1,1,2,2-tetrachloroethane is added to the product as an internal standard. Finally the products are characterized by ¹H NMR spectroscopy in DMSO-d₆ solvent. In addition to ¹H NMR analysis, gas chromatography studies are also carried out to identify the products formed and determine the yield.

Spectral data for ¹H NMR

Biphenyl⁹

¹H NMR (CDCl₃) δ 7.38-7.42 (m, 2H), 7.48-7.54 (m, 4H), 7.63-7.68 (m, 4H).

4-Me substituted biphenyl⁹

¹H NMR (CDCl₃) δ 2.35 (s, 3H), 7.16 (d, *J* = 7.55 Hz, 2H), 7.22-7.29 (m, 1H), 7.33 (t, *J* = 7.22 Hz, 2H), 7.38 (d, *J* = 7.36 Hz, 2H), 7.38 (d, *J* = 7.56 Hz, 2H), 7.49 (d, *J* = 7.36 Hz, 2H).

4-OMe substituted biphenyl⁹

¹H NMR (CDCl₃) δ 3.83 (s, 3H), 6.93 (d, *J* = 8.61 Hz, 2H), 7.28 (t, *J* = 7.35 Hz, 1H), 7.36 (t, *J* = 7.35 Hz, 2H), 7.45-7.50 (m, 4H).

4-COMe substituted biphenyl⁹

¹H NMR (CDCl₃) δ 2.65 (s, 3H), 7.36-7.48 (m, 3H), 7.60-7.67 (m, 4H), 8.02 (d, *J* = 8.41 Hz, 2H).

4-NO₂ substituted biphenyl⁹

¹H NMR (CDCl₃) δ 8.30 (d, *J* = 8.83 Hz, 2H), 7.72 (d, *J* = 8.83 Hz, 2H), 7.66-7.62 (m, 2H), 7.55-7.51 (m, 2H), 7.48-7.44 (m, 1H).

4-OH substituted biphenyl^{11b}

¹H NMR (CDCl₃) δ 6.91 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 7.3 Hz, 2H).

2-Me substituted biphenyl^{19a}

¹H NMR (CDCl₃) δ 2.30 (s, 3H), 7.15-7.20 (m, 4H), 7.30-7.35 (m, 3H), 7.40-7.54 (m, 4H).

4-Cl substituted biphenyl^{19a}

¹H NMR (CDCl₃) δ 7.35-7.47 (m, 5H), 7.52-7.63 (m, 4H).

4-Br substituted biphenyl^{19a}

¹H NMR (CDCl₃) δ 7.41-7.53 (m, 5H), 7.63-7.73 (m, 4H).

4-I substituted biphenyl^{19a}

¹H NMR (CDCl₃) δ 7.44-7.57 (m, 5H), 7.68-7.83 (m, 4H).

4-COOH substituted biphenyl^{19a}

¹H NMR (DMSO-d₆) δ 7.40 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H)

2-Phenylnaphthalene^{1a}

¹H NMR (DMSO-d₆) δ 7.38 (t, *J* = 7.3 Hz, 1H), 7.45-7.57 (m, 3H), 7.71-7.77 (m, 3H), 7.85-7.98 (m, 3H), 8.04 (s, 1H).

1-Phenyl-2,4,6-trimethylbenzene^{19d}

¹H NMR (DMSO-d₆) δ 2.38 (s, 9H), 6.82 (s, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H).

Results and Discussion

The molecular weight of the MMA-GMA copolymer determined by size-exclusion chromatography is *ca.* 160000. The molecular weight of the copolymer can be controlled by optimizing the amount polymerization initiator, AIBN as well as the temperature of reaction. A higher amount of AIBN and high temperature results in a vigorous reaction and hence the molecular weight of the polymer is lower. The inclusion of glycidyl groups into the polymer framework has been confirmed by ¹H NMR spectroscopy, which shows that the amount of GMA in the product is *ca.* 11 mole%. Monoliths are prepared from this copolymer by thermally induced phase separation from a mixture of 4:1 ethanol and water. Amine functional groups are introduced into the polymer backbone by aminolysis of the epoxy groups present in the framework followed by their Schiff-base condensation with salicylaldehyde. The salen type of donor sites, thus, introduced into the framework bind with Pd(II) to give **Pd-SBAM**. The FT-IR spectra of the monolith in various stages, starting from the MMA-GMA copolymer to Pd-containing monolith (**Pd-SBAM**) are shown in Fig. 1. It can be seen that a band at around 3300 cm⁻¹ appears in the spectrum of the aminolyzed product (Fig. 1b) due to the presence of -NH₂ group which is absent before the aminolysis, in the MMA-GMA copolymer (Fig. 1a). In case of Schiff-base functionalized polymer (Fig. 1c), the band due to the presence of -NH₂ group disappears. Simultaneously, a sharp band at 1635 cm⁻¹ appears confirming the presence of C=N moiety which is generated from the Schiff-base condensation between the amine group of the monolith and the aldehyde. The Pd containing monolith, **Pd-SBAM**, also shows the band at 1628 cm⁻¹ (Fig. 1d) confirming the retention of Schiff-base functionality in the material. The presence of Pd in the functionalized monolith has been confirmed by ICP-AES analysis. For this purpose, known amount of the catalyst monolith is digested in concentrated nitric acid and the metal is

extracted quantitatively in known volume of water. The Pd content has been calculated to be 0.0277 mmol/g of the material.

To understand the morphology of the surface of the monoliths at different stages, their microstructures have been studied by scanning electron microscopy (SEM). SEM images of copolymer monolith, Schiff-base functionalized monolith and **Pd-SBAM** are given in Fig. 2. The SEM image of MMA-GMA monolith (Fig. 2a) reveals the formation of a continuous interconnected network of macropores with skeleton size for the microstructures *ca.* 0.6-1.0 μm and pore sizes between 2.5-3.0 μm . The skeleton size of the polymer monoliths is reliant on two parameters: molecular weight of the copolymer and cooling temperature for phase separation. With the increase in molecular weight and decrease in cooling temperature, the skeleton size decreases. Apart from this, the solvent ratio also played an important role in the control of the skeleton size and hence the microstructure of the monoliths. SEM images of Schiff-base functionalized monolith and **Pd-SBAM** (Fig. 2b and c, respectively) also show similar interconnected network morphology witnessing the stability of the monolith during its journey to the formation of Pd catalyst, **Pd-SBAM**.

Catalysis

The ability of **Pd-SBAM** to act as an efficient catalyst in C-C bond forming reactions has been examined. The monoliths have been employed as catalyst in Suzuki-Miyaura cross-coupling (SMC) reaction of aryl halides with derivatives of phenylboronic acid. There are several parameters which have been tuned to get the optimized yield. The reactions have been performed with 1.0 mmol of bromobenzene and 1.2 mmol of phenyl boronic acid in the presence of 2.5 mmol of base under varying conditions *e.g.* using different solvents, temperature, various bases *etc.* The amount of catalyst taken for the reaction is 0.02 g, which has been chosen after carrying out few reaction cycles with varying amount of catalysts. Though an amount less than this gives less yield of the product, increasing the amount does not affect either the rate or yield of the reaction. The first step in the optimization study is to ascertain the effect of various solvents on the SMC reaction. Water is the most desirable solvent from environmental view point used in any chemical reaction. The reactions have been carried out in the presence of different solvents *viz.* DMF, MeOH and H₂O and 1:1 mixtures of DMF/H₂O and MeOH/H₂O using potassium carbonate as the base at 333 K; and the results are given in Table 1 (Entries 1-5).

While the reactions give much low yield when DMF or MeOH (Table 1, entries 1 and 3) are taken solely as the solvents, the yield is very high *ca.* 98.0-99.0 % when 1:1 mixtures of these solvents in water are taken. For water alone, the conversion is somewhat less than that in solvent mixtures but such marginal decrease in yield is outweighed by the fact that no harmful organic waste is produced as the side product.

Next, the coupling reactions are carried out at different temperatures varying from 298 K to 343 K using K_2CO_3 as base in aqueous medium (Table 1, entries 5-9). The yield of the reaction increases with increase in temperature. The best result is obtained with 98.8 % yield at 343 K, which is the highest temperature chosen for the study. Thus we see that with increase in the temperature the conversion percentage increases. But for the present study 333 K has been chosen as the optimized temperature instead of 343 K, since in that case there will be minimal compromise on the yield but the temperature is moderate. SMC reactions are generally carried out in the presence of a base as a co-catalyst, which apart from neutralizing the acidic by-products formed during the reaction (HX, where X= halide) increase the catalytic activity. Thus, a careful choice of base which is reactive as well as cost-effective is therefore essential.

Different bases have been engaged for SMC reactions using **Pd-SBAM** as catalyst in water at 333 K. The results are given in Table 1 (Entries 5, 10-20). A good yield is obtained when potassium carbonate (95.7%), potassium tertiary-butoxide (91.2%) and cesium carbonate (98.5%) are used. When the reactions are carried out in presence of other bases, yields vary from 17.1 to 72.8%. To perform rest of the SMC reactions, K_2CO_3 has been selected because of its lower price compared to Cs_2CO_3 . Finally, SMC reactions have been carried out using different derivatives of phenylboronic acid with bromobenzene in the presence K_2CO_3 in water at 333 K. The results given in Table 1 (Entries 5, 21-22) indicate that among the other derivatives, phenylboronic acid gives the best result. With the increase in number of methyl group(s) in phenyl ring of the boronic acid derivatives, yield of the SMC reaction decreases.

After careful tuning of all the reaction parameters, SMC reactions are carried out between a series of different bromo/iodobenzene derivatives and phenylboronic acid in water at 333 K using K_2CO_3 as base. The results have been shown in Table 2. It is evident that most of the substrates show very good yield (above 90%) within 5-6 h of reaction. Yield varies from 85.2 to 99.2% with high turnover number (TON). The aryl halides which have been studied as substrates contain both electron withdrawing and electron donating substituents. Iodobenzene and

bromobenzene show comparable conversion, but reactions carried out with chlorobenzene under identical conditions do not proceed at all. SMC reactions involving chlorobenzene would be highly desirable^{31,32} as substrate since it is much cheaper than the bromo/iodo derivative. However, when the reactions with 4-nitrochlorobenzene and phenylboronic acid are carried out at a higher temperature (343 K) with 10 times amount of the catalyst for a prolonged period (24 and 36 h) the conversion is *ca.* 11 and 13 %, respectively. The values are very small compared to that obtained for bromo/iodo derivatives. A reaction temperature higher than this is undesirable as it affects the morphology of the monolithic catalyst and hence its recyclability.

Hot Filtration and Leaching Test:

To test for heterogeneity of the catalyst, *i.e.* whether **Pd-SBAM** truly functions in a heterogeneous catalyst, hot filtration test has been carried out on SMC reaction of bromobenzene. During the catalytic SMC reaction, **Pd-SBAM** is separated under hot condition from the reaction mixture after 2 h and the reaction is continued for the usual duration. Fig. 3 shows the plot of yield *versus* reaction time for a hot-filtration experiment and a normal uninterrupted catalytic experiment using **Pd-SBAM** as the catalyst. The results show no increase in the conversion after 2 h in case of hot filtration test (Fig. 3b), *i.e.* after the catalyst is separated. On the other hand, the uninterrupted catalytic reaction shows increase in conversion (Fig. 3b), as expected. This indicates that C-C bond forming reaction is catalyzed by the presence of Pd catalyst. Furthermore, the reaction mixture collected after filtration is examined for its Pd-content by ICP-AES analysis and the results confirmed the presence of Pd below detectable limit. Thus we can infer that Pd is not leached out from the catalyst and it is the polymer bound Pd which is responsible for the catalytic activity.

Recyclability and Effect of Inert Atmosphere

The most attractive property of a heterogeneous catalyst is its recyclability. In order to study the reusability of the catalyst, **Pd-SBAM** was recovered after each run, washed by sonication in 1:1 mixture of ethanol/water under cold condition and dried in vacuum. Then the same catalyst is used for the next run under identical reaction conditions. A plot of conversion percent *versus* the number of reaction cycle for SMC reaction of bromobenzene and phenylboronic acid in the presence of potassium carbonate at 333 K has been given in Fig. 4. It

can be seen that the catalyst can be used at least up to five cycles in the C-C bond formation reaction without appreciable loss of its activity. In this pertinent to mention here that apart from air, the reusability of the catalyst has been checked under identical condition in argon as well. The yield of SMC reaction is 95.7% when fresh catalyst is used while it is 94.0% with the recovered catalyst in the fifth reaction cycle. On the other hand, the corresponding values in argon medium are 96.0 and 85.1% for first and fifth cycle, respectively. In argon atmosphere activity of the catalyst is lost significantly from the third cycle onwards. Thus, presence of oxygen plays a crucial role as far as the reusability of the catalyst is concerned. Aerial oxidation not only effectively suppresses the reduction of Pd(II) to Pd(0), it also prevents the agglomeration of Pd(0) to Pd black nanoparticles.¹³ The pictures of the fresh and used catalyst (ball-milled) along with their corresponding SEM images are given in Fig. 5. The images confirm the retention of the microstructure of the monolith even after five reaction cycles (Fig. 5b). Whereas, comparison of the color contrast of the fresh and used samples, suggests somewhat darkening of the color of the used material (Fig. 5b) over the fresh one (Fig. 5a) due to formation of black colored Pd(0) particles.

Mechanism

A possible reaction mechanism for the SMC reaction using **Pd-SBAM** as the catalyst is given in Scheme 2. It is expected that the Pd(II) present in **Pd-SBAM** is at first reduced to Pd(0) probably by phenylboronic acid in the presence of a base.¹ This Pd(0) nanocatalyst (**I**) formed *in situ* in the reaction mixture actually acts as the active center in this C-C bond forming reaction. In the next step, insertion of the Schiff base bound Pd(0) takes place in between the carbon-halogen bond of aryl halide (Ar-X) to form (**II**). Due to this oxidative addition the oxidation state of Pd(0) changes to Pd(II). Then, in presence of base, the phenyl group from phenylboronic acid replaces the halogen atom from the complex (by rupture of Pd-X bond) to form a Pd-C bond with palladium (**III**). In the ultimate step, this phenyl group migrates to form a bond with the aryl group *via* formation of a C-C bond leading to the final biphenyl product with the regeneration of the Pd(0) species bound to the Schiff base sites (**I**) in the monolith. This leads to the original material ready to catalyze the insertion of another aryl halide to initiate a new cycle. Generation of Pd(0) during the reaction cycle is confirmed by XPS analysis of the **Pd-SBAM** monolith before and after (five cycles) catalysis. The results obtained are shown in Fig. 6. It is clear from

the figure that in both the materials there is a peak at around binding energy value of 337.5 eV, which is attributed to the presence of Pd²⁺ species bound to the Schiff base sites. But in the used catalyst another band at around 335.6 eV can be seen (Fig. 6b) consistent with the presence of Pd(0) which is absent in the fresh catalyst (Fig. 6a). Apart from that, TEM analyses of the catalyst, after one reaction cycle and five reaction cycles have been done. The images shown in Fig. 7 indicate the formation of Pd(0) in both the catalysts; in case of the material used for one reaction cycle the size of Pd-nanoparticles are *ca.* 2-3 nm (Fig. 7a), whereas the catalyst after five reaction cycle shows particle size of *ca.* 8-12 nm (Fig. 7b). Thus we see a growth in the particle size after reuse of the catalyst for several times.

Conclusions

In the present study we have discussed about the synthesis of a macroporous MMA-GMA copolymer monolith and its subsequent functionalization to generate a stable Pd-containing catalyst, **Pd-SBAM**. It shows excellent catalytic activity towards SMC reaction for a variety of substrates with high yield. The most attractive feature is that the reactions can be carried out under aerobic condition and in the presence of water as the solvent. Characterization of the materials carried out at every step shows interconnected network morphology and its preservation throughout the functionalization and catalytic process. Apart from being in the form of a monolith, which facilitates easy separation of the catalyst from the reaction mixture, macroporous interconnected network performs as an excellent catalyst support. It is worthy to mention that the catalytic properties would have been more useful if the C-C bond formation reactions could be executed with chloroderivatives as substrates, which is much more economic compared to the bromo/iodo counterparts. Thus, the present target is to design those polymer based Pd containing catalysts which can catalyze such reactions. Apart from that, the activity of **Pd-SBAM** in other C-C bond formation reactions shall also be explored.

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Legend for schemes and figures

Scheme 1. General protocol for the synthesis of **Pd-SBAM**: (a) 1.0 mol of **I** + 2.5 mol of ethylenediamine; Solvent: Methanol, Temperature: 328 K, Time 4 h. (b) **II** + 2.0 mol of salicylaldehyde; Solvent: Methanol, Room Temperature, Time: 12 h. (c) **III** + Palladium(II) acetate solution, Solvent: Toluene, Room Temperature, overnight.

Scheme 2. Possible reaction pathway of SMC reaction catalyzed by **Pd-SBAM**.

Fig. 1. FT-IR spectra of (a) MMA-GMA copolymer monolith, (b) aminolyzed MMA-GMA copolymer monolith, (c) Schiff-base functionalized monolith and (d) **Pd-SBAM**.

Fig. 2. SEM images of (a) MMA-GMA copolymer monolith, (b) Schiff-base functionalized monolith and (c) **Pd-SBAM**.

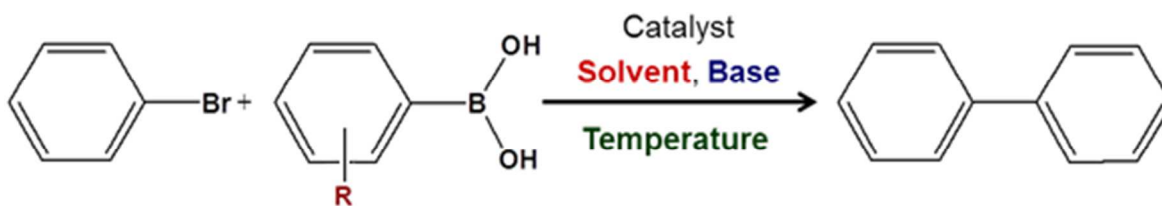
Fig. 3. Plot of yield *versus* reaction time for (a) hot-filtration experiment and (b) normal uninterrupted catalytic experiment using **Pd-SBAM** as the catalyst.

Fig. 4. Recycling efficiency for SMC reaction of bromobenzene and phenylboronic acid in (a) air and (b) argon at 333 K.

Fig. 5. SEM images of (a) fresh and (b) used (five times) catalysts. Inset: Corresponding digital pictures of ball-milled catalysts.

Fig. 6. X-ray photoelectron spectra of (a) fresh and (b) used catalysts.

Fig. 7. SEM images of (a) fresh and (b) used (five times) catalysts.

Table 1: SMC reactions under different conditions

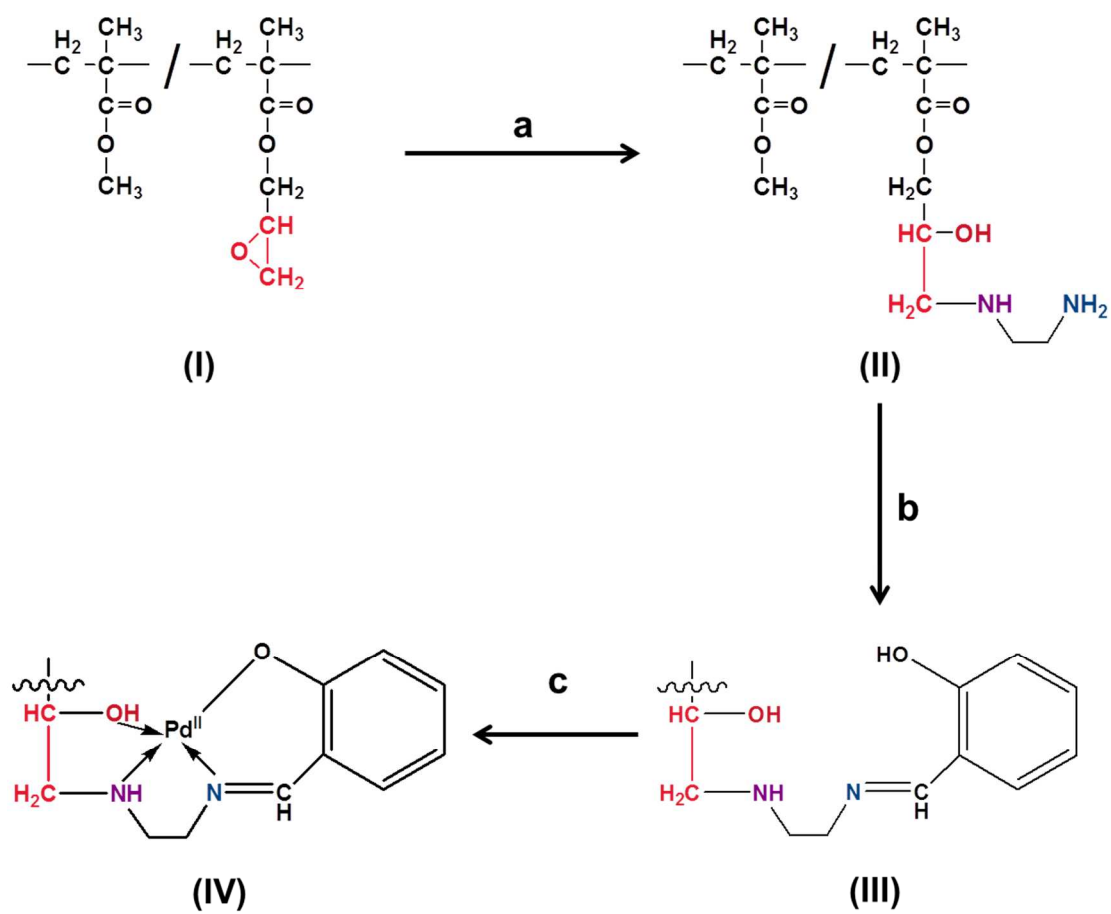
Entry	Solvent	Base	Temperature	R	Time (h)	Yield (%)	Turn over number (TON)
1.	DMF	K ₂ CO ₃	333 K	H	5	34.0	614
2.	DMF/H ₂ O	K ₂ CO ₃	333 K	H	4	99.0	1788
3.	MeOH	K ₂ CO ₃	333 K	H	5	68.0	1228
4.	MeOH/H ₂ O	K ₂ CO ₃	333 K	H	4	98.0	1770
5.	H ₂ O	K ₂ CO ₃	333 K	H	5	95.7	1728
6.	H ₂ O	K ₂ CO ₃	298 K	H	5	12.5	225
7.	H ₂ O	K ₂ CO ₃	313 K	H	5	21.7	391
8.	H ₂ O	K ₂ CO ₃	323 K	H	5	78.0	1408
9.	H ₂ O	K ₂ CO ₃	343 K	H	5	98.8	1784
10.	H ₂ O	Li ₂ CO ₃	333 K	H	5	17.1	308
11.	H ₂ O	Na ₂ CO ₃	333 K	H	5	72.8	1315
12.	H ₂ O	NaHCO ₃	333 K	H	5	37.5	677
13.	H ₂ O	NaOH	333 K	H	5	39.2	708
14.	H ₂ O	NaOAc	333 K	H	5	17.4	314
15.	H ₂ O	KHCO ₃	333 K	H	4	41.5	749

16.	H ₂ O	K ₃ PO ₄	333 K	H	5	72.7	1313
17.	H ₂ O	KF	333 K	H	4	21.1	381
18.	H ₂ O	^t BuOK	333 K	H	5	91.2	1647
19.	H ₂ O	NEt ₃	333 K	H	5	32.7	590
20.	H ₂ O	Cs ₂ CO ₃	333 K	H	5	98.5	1779
21.	H ₂ O	K ₂ CO ₃	333 K	4-CH ₃	5	88.4	1596
22.	H ₂ O	K ₂ CO ₃	333 K	2,4,6-CH ₃	5	63.4	1145

Table 2: SMC reaction over different substrates under optimized reaction condition

Entry	R	X	Time (h)	Yield (%)	Turn over number (TON)	Turn over frequency (TOF)
1.	H	Br	5	95.7	1728	354
2.	H	I	5	98.3	1775	355
3.	4-CH ₃	Br	5	96.5	1743	348
4.	4-CH ₃	I	5	99.2	1791	358
5.	4-OCH ₃	Br	5	97.1	1753	350
6.	4-OCH ₃	I	5	98.6	1781	356
7.	4-COCH ₃	Br	6	91.3	1649	274
8.	4-COCH ₃	I	6	92.7	1674	279
9.	4-NO ₂	Br	6	90.2	1629	271
10.	4-NO ₂	I	6	92.8	1676	279
11.	4-OH	Br	5	93.9	1696	339
12.	2-CH ₃	Br	5	94.8	1712	342
13.	4-Cl	Br	5	90.5	1634	326
14.	4-Br	Br	5	96.6	1744	348
15.	4-I	Br	5	98.0	1770	354
16.	4-COOH	Br	6	92.6	1672	278
19.		Br	6	89.0	1607	267
20.		Br	6	85.2	1539	256

Scheme 1



Scheme 2

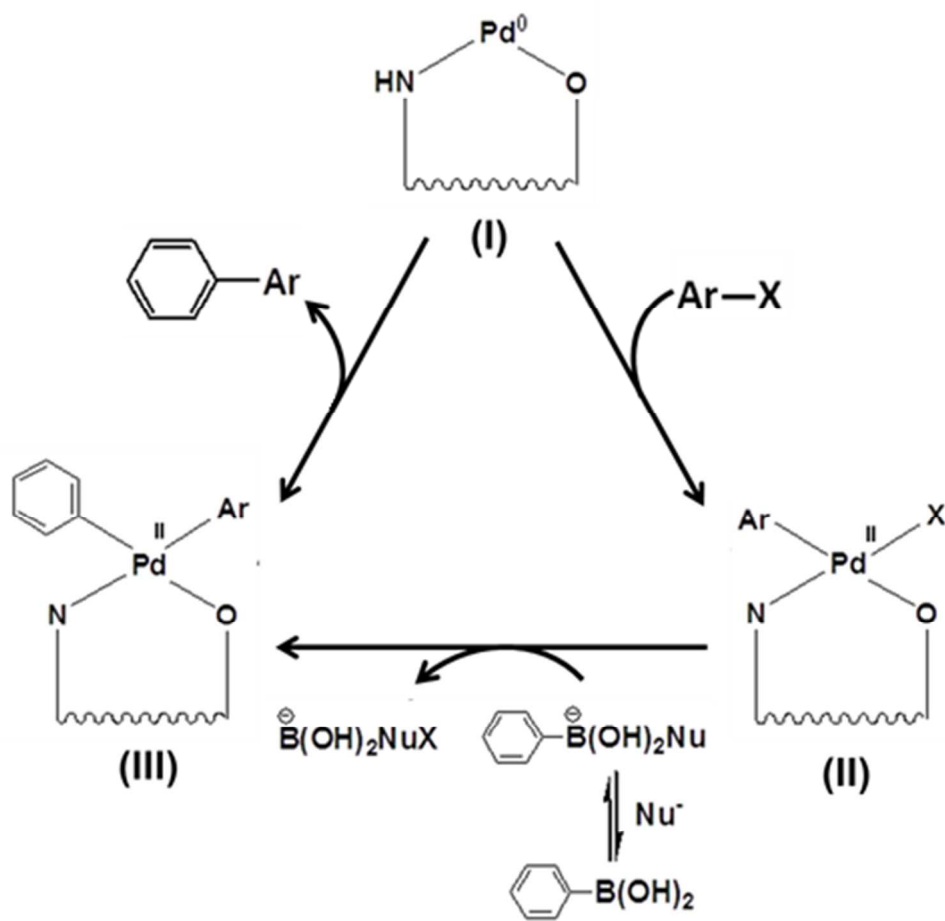


Fig. 1

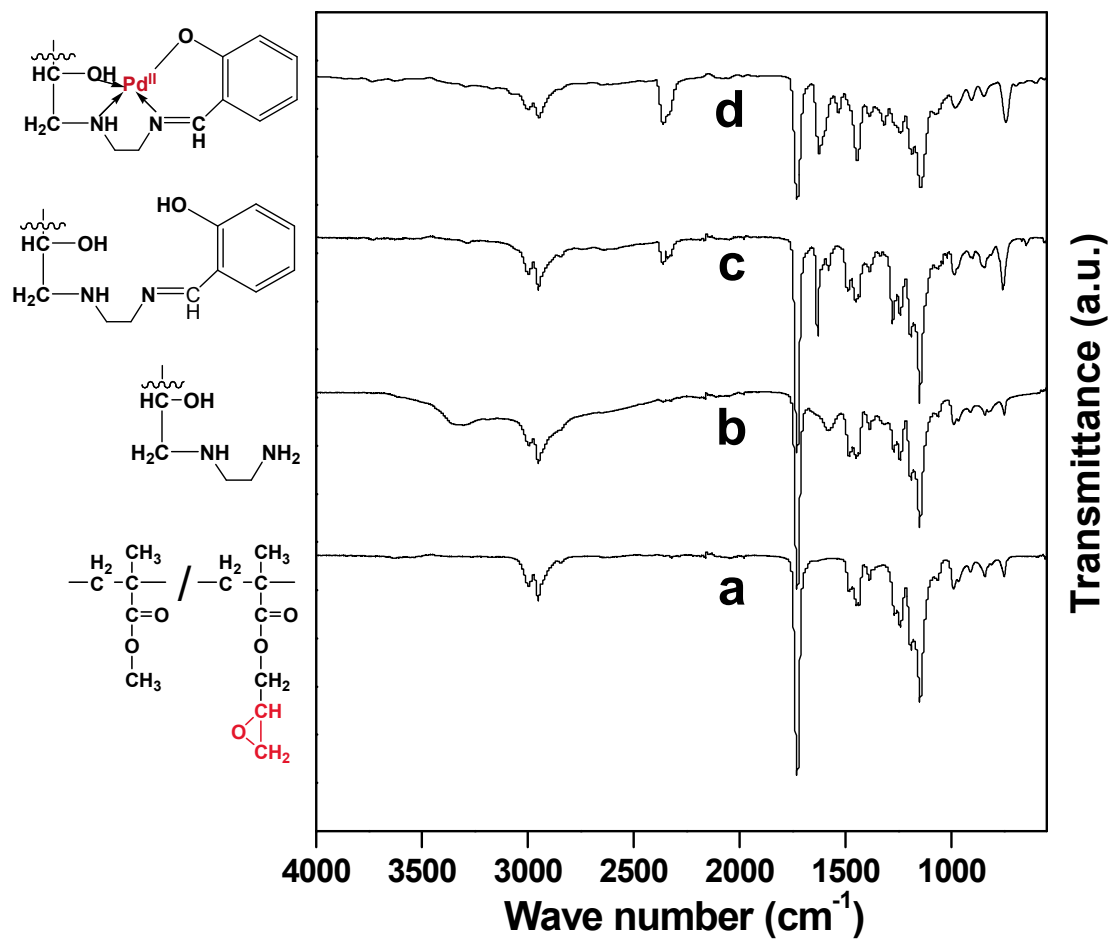


Fig. 2

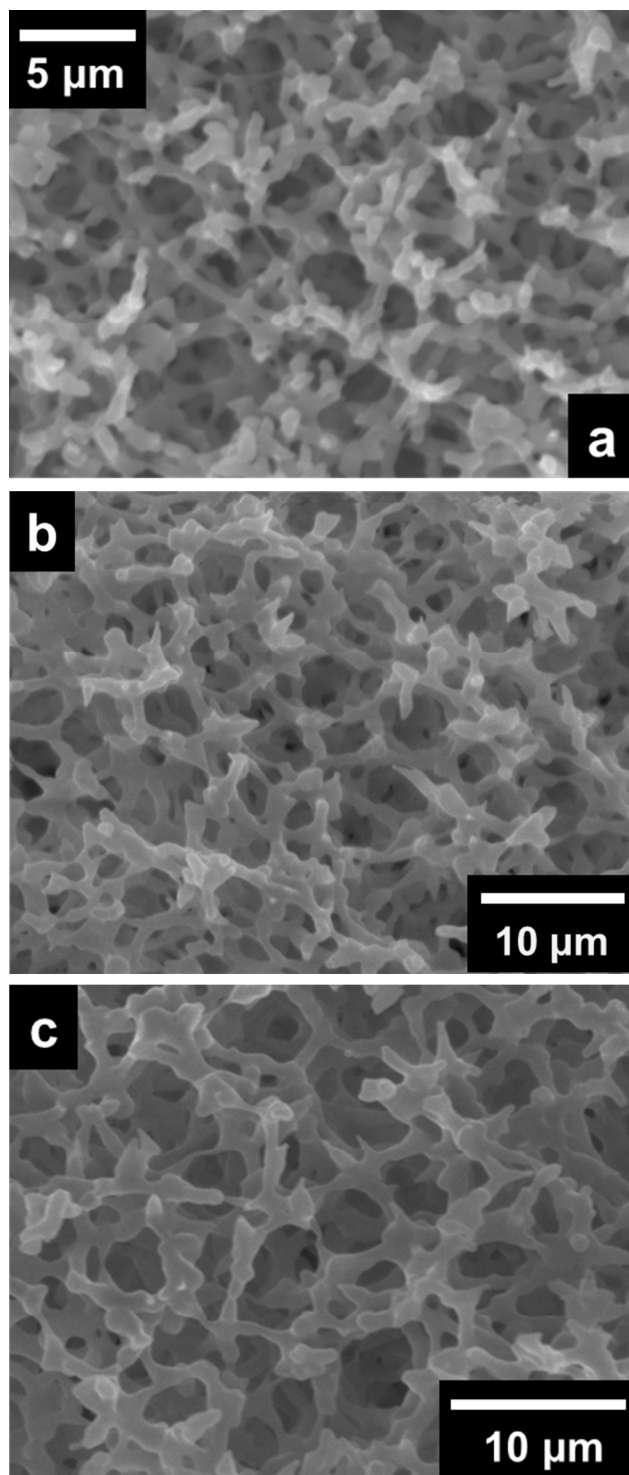


Fig. 3

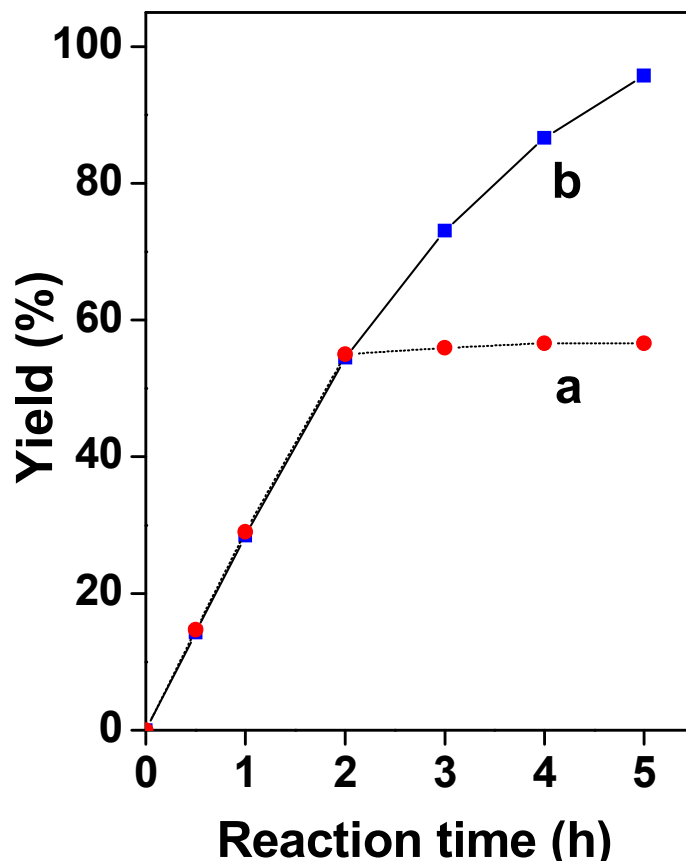


Fig. 4

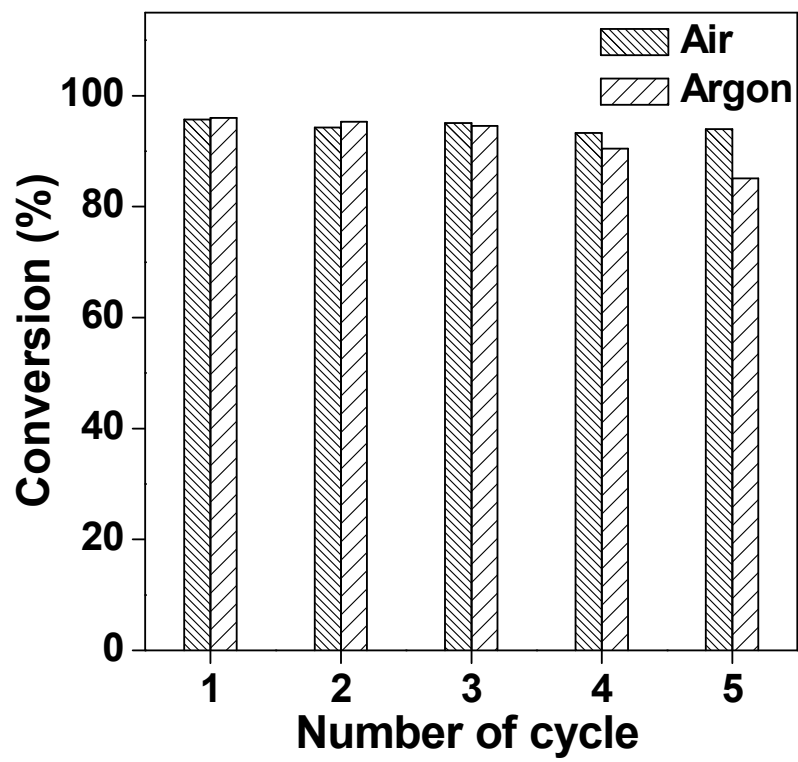


Fig. 5

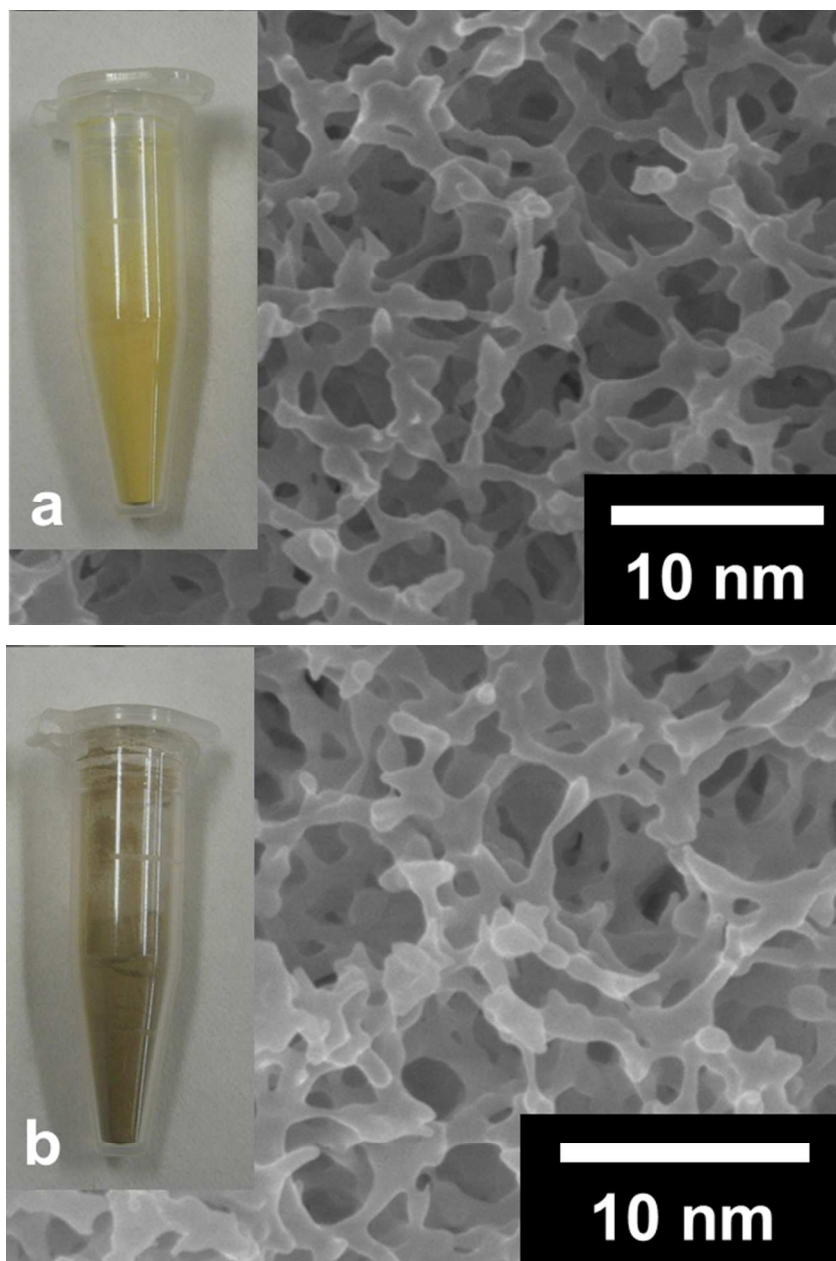


Fig. 6

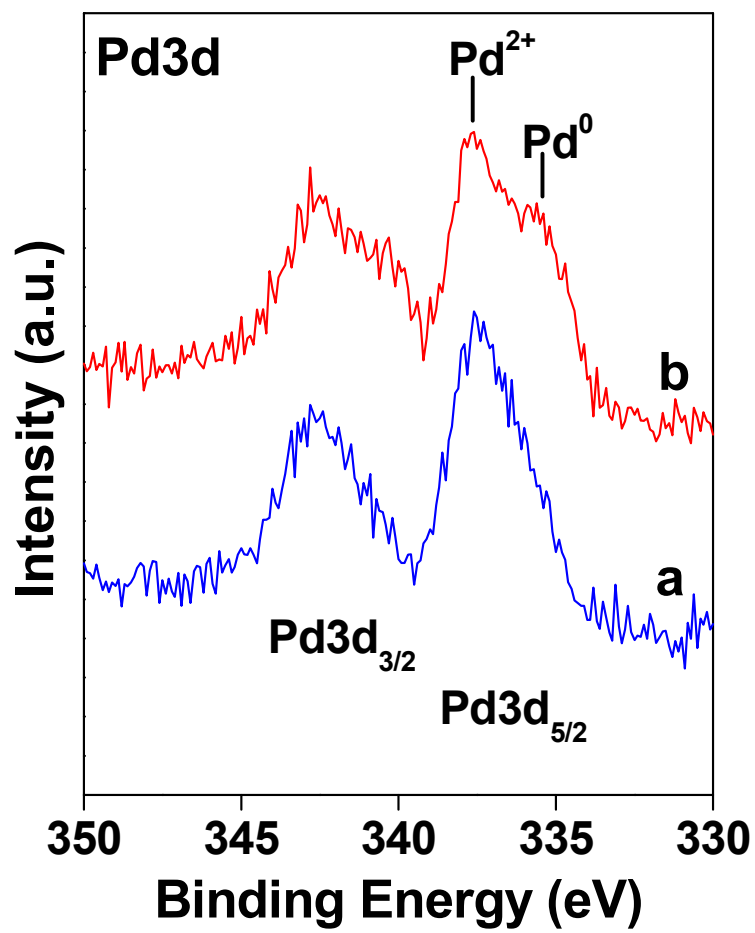
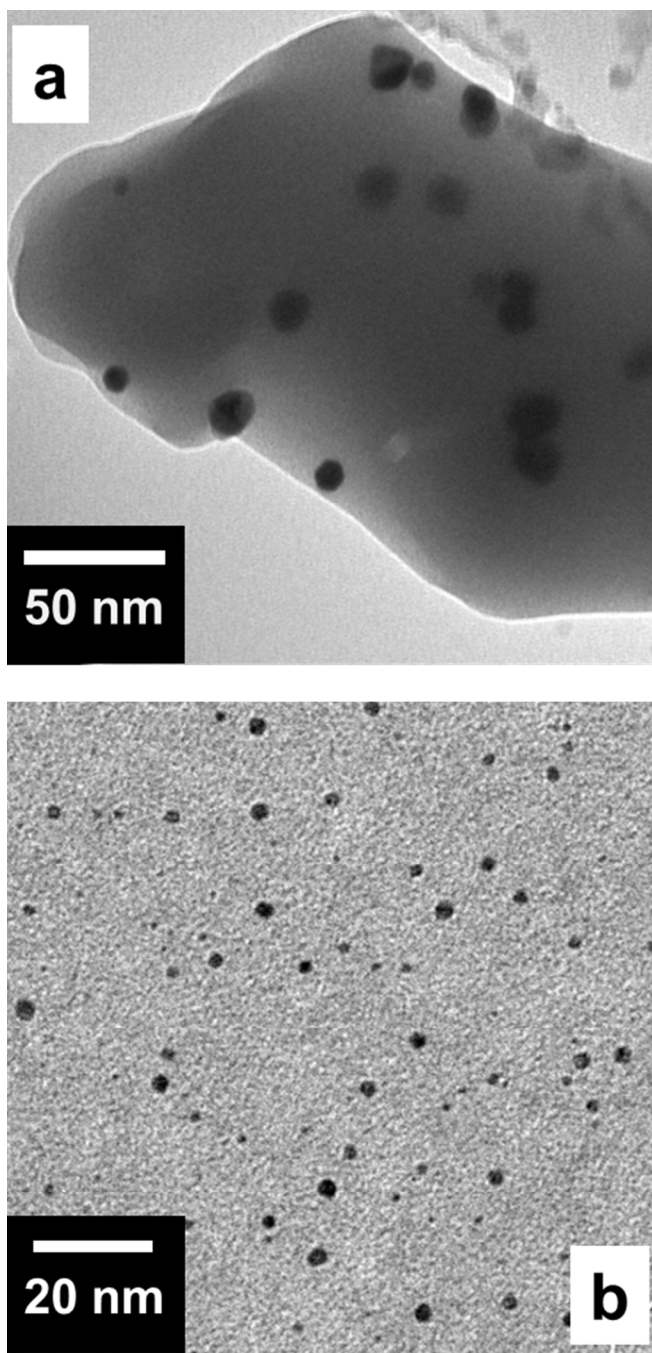


Fig. 7



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