

Introducing of a New Bio-inspired Hierarchical Porous Silica as an Inorganic Host for Ni–Pd Alloy Nanoparticles for the Synthesis of Aminobiphenyls from the One-Pot Suzuki–Miyaura Coupling-Nitro Reduction

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Received: 1 April 2018 / Accepted: 10 June 2018 © Springer Science+Business Media, LLC, part of Springer Nature 2018

Abstract

This work reports a facial way to synthesize of an efficient catalyst based Ni–Pd alloy nanoparticles which supported on a new bio-inspired hierarchical porous silica and its catalytic activity in the one-pot Suzuki–Miyaura cross coupling-nitro reduction. The synthesized catalyst was fully characterized by FT-IR, XRD, FESEM–EDX, elemental mapping, TEM, ICP-AES, N₂ adsorption–desorption, DRS–UV–Vis and XPS techniques. Use of inexpensive catalyst, high yields of the products and reusability of the catalyst are some of the advantages of our procedure.

Graphical Abstract



Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-018-2457-6) contains supplementary material, which is available to authorized users.

Extended author information available on the last page of the article

Keywords Pd–Ni alloy nanoparticles · Suzuki–Miyaura-nitro reduction · Heterogeneous catalysis · Luffa · Aminobiphenyls · Hierarchical porous silica

1 Introduction

Among various noble metal nanoparticles (NPs), palladium NPs are widely used as a catalyst in many important organic reactions, owing to high activity, small size and high surface area. However, the limited sources and high price of these NPs were prevented from their practical applications. There are many effective strategies to break these barriers, which one of them is the minimum usage of Pd NPs through the combining of inexpensive transition metals like Ni, Fe, Co and Cu into Pd to form alloys [1–3]. Lattice strain, local coordination environmental and electronic effects between the second metal and Pd NPs can appear the special properties in alloys [4]. Among various inexpensive transition metals, Ni has attracted many research attentions in order to be alloyed with Pd. Many studies have shown that the addition of Ni into Pd enhance its catalytic activity in comparison with the pure Pd, due to the synergistic effect between Pd and Ni [5, 6]. Another alternative approach is increasing the specific surface area via immobilizing of Pd NPs on the special supports such as porous silica [7], carbon nanotube [8] and graphene [9]. It is important to note that, using of supports make catalysts more stable and possible to reuse them for several times. In this regards, if we can design suitable support for Pd NPs, the catalytic performance and stability of them will be extremely improved in organic reactions.

Biological templates are very important for the synthesis of biomimetic and bioinspired materials with novel structures. Many biological materials such as plant leaves and roots, viruses, bacteria cells, diatoms, eggshells, sea urchins, spider silks, wood, fibers, pollens, and insects have been used for the synthesis of biomimetic materials [10, 11]. These materials with various morphologies were used in different application such as preparation of catalysts [12], gas sensors [13], solar cells and electrodes for batteries [14].

Luffa cylindrica sponge is a tropical and subtropical climber vine plant from the family of *Cucurbitaceae*. Recently, Luffa has attracted tremendous research attention because of the special properties including abundancy, low cost, low density, environmentally benign and unique structure. This sponge has the netting-like fibrous vascular systems. These systems are constructed from the continuous micro and mesochannels which form a hierarchical pore structure. The different size of these channels is related to their growing areas. Many studies on Luffa have presented that it can be used as water absorption [15], composite materials [16], scaffolds for tissue engineering [17], supercapacitor or battery [18], wastewater usage [19], fuel cells [20], matrix, reinforcement and catalytic reactor [21, 22].

Aromatic amines especially aminobiphenyls are a very important class of organic compounds due to extensive applications in dyes [23], medicine [24] and catalysts [25]. Numerous methods exist for the preparation of aminobiphenyls, which the most common method is involving two steps: the first step is the preparation of nitrobiphenyls from the Suzuki-Miyaura reaction between nitro aryl halides and phenylboronic acids in the presence of Pd catalysts, and the second step is the reduction of nitrobiphenyls to aminobiphenyls by using of hydrogen gas [26] or reducing agents such as sodium borohydride [27, 28], silanes [29], formats [30] and hydrazine hydrate [31-33]. It is noteworthy that, the preparation of aminobiphenyls from the coupling reaction of amino aryl halides is not popular because the aryl halides with electron donating group have a difficult oxidative addition step [34]. There are some reports, about the synthesis of aminobiphenyls via the one-pot Suzuki-Miyaura cross coupling-nitro reduction by conventional and microwave heating [35-38]. Although these reports provide an improvement but there are some disadvantages such as high temperatures, expensive catalysts, long reaction times and high amount of catalysts.

In this work, we introduce a simple process for the preparation of a novel hierarchical porous silica using Luffa as a biotemplate (BIHPS). The synthesized hierarchical porous silica was used as a suitable support for Ni–Pd alloy NPs. Then, we report a facial method for the synthesis of aminobiphenyls in the presence of Ni₇–Pd₃@BIHPS containing 0.19 mol% Pd and 0.43 mol% Ni through the one-pot Suzuki–Miyaura coupling-nitro reduction by conventional heating. Also, in this work hydrazine hydrate was used as an environmentally friendly reducing agent in order to reduction of nitro groups because of producing water and nitrogen as by-products.

2 Experimental Section

2.1 Reagents and Instrumentation

The Luffa sponge used in this work were collected from the Guilan privacy in northern Iran. All chemicals were purchased from Aldrich, Fluka and Merck in high purity. The purity of the substrates and products were monitored by thin layer chromatography (TLC) on 60 F254 silica gel plates.

Fourier-transform infrared spectra (FTIR) were carried out on Perkin Elmer RX1 in KBr matrix. X-ray powder diffractions (XRD) were recorded on a PHILIPS PW1730 X-ray diffractometer using Ni-filtered Cu-Kα radiation $(\lambda = 0.15418 \text{ nm})$. Field emission scanning electron microscopy (FESEM) was performed on a TESCAN MIRA instrument. Transmission electron microscopy (HRTEM) using a JEOL, JEM-2100F, 200 kV TEM. The pore size and specific surface areas studies by Brunauer–Emmett–Teller (BET) theories were carried out using nitrogen adsorption–desorption measurement at liquid nitrogen temperature on an SBELSORP MINI instrument. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific, ESCALAB 250Xi Mg X-ray resource. Diffuse reflectance spectra (DRS) were performed on a Scinco 4100 apparatus. Nickel and palladium concentrations of samples were determined by ICP-AES Arcos EOP. ¹HNMR and ¹³CNMR spectra of the products were recorded by a Bruker Advanced 300 spectrometer.

2.2 Preparation of Bio-inspired Hierarchical Porous Silica (BIHPS)

Luffa cylindrica fruits were collected, peeled off, washed several times with distilled water to remove the dirt and dust particles and dried in air for 3 days. The chemical composition analysis showed that the components of this sponge are cellulose 56.10%, lignin 11.88% and hemicellulose 29.91% (Table S1). In order to increase the surface area and pore volume of Luffa, removal of lignin and hemicellulose are necessary through alkalization (KOH) treatment. After smashing and sieving (60 mesh size), the obtained powder was immersed in an alkaline solution of KOH (11 g of powder in 100 mL of 8 M KOH) for 24 h at 80 °C. Then the mixture was filtered and washed sequentially with water and kept at 100 °C for overnight. In order to the replication process using a sol-gel method, 1 g of KOH-treated Luffa was dispersed in 30 mL deionized water and stirred for 20 min. Then, tetraethylorthosilicate (3.5 g, 16.8 mmol) was added. The sol-gel process was carried out under vigorously stirring for 48 h at room temperature and kept at romp temperature for 72 h. The resultant gel was filtered and washed with deionized water and dried under vacuum at 60 °C for 24 h. Finally, for removing of Luffa template, the sample was calcined at 550 °C for 6 h and BIHPS as a white powder was synthesized. It is important to note that, in the synthesis process of BIHPS, we used both KOH treated Luffa and raw Luffa (Luffa without KOH treated), separately. N2 adsorption-desorption was carried out for both prepared BIHPS for comparison, and the results showed that the pore volume and surface area of BIHPS which synthesized using of KOH treated Luffa is higher than the other one (Fig. S1 and Table S2). So, we continued the synthesis of catalysts in this work by using of KOH treated luffa.

2.3 Preparation of Ni–Pd Alloy NPs Supported on Bio-inspired Hierarchical Porous Silica (Ni₇– Pd₃@BIHPS)

At first, an aqueous solution of NiCl₂ (0.0026 g in 3.0 mL water) and BIHPS (0.1 g in 5.0 mL water) were mixed for 20 min. Then, an aqueous solution of PdCl₂ (0.0017 g in 3.0 mL water) was added and stirred for 5 h at room temperature. The obtained solution was placed in an ultrasonic bath (25 kHz) for 15 min. After sonication, an aqueous solution of NaBH₄ (0.1 M, 5.0 mL) was injected dropwise to the mixture along 2 h at 60 °C and the suspension was stirred for extra 4 h. Finally, the catalyst was filtered, washed with water and methanol and dried at 70 °C for 5 h (Scheme 1). ICP-AES estimated 0.066 mmol g⁻¹ Pd and 0.145 mmol g⁻¹ Ni content of Ni_{6.9}–Pd_{3.1}@BIHPS.

2.4 Preparation of Aminobiphenyls in the Presence of Ni₇-Pd₃@BIHPS

Aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2.0 mmol), Ni_7 –Pd₃@BIHPS (0.03 g) and H_2O/DMF (2:1, 3 mL) were mixed and heated at 80 °C for an appropriate time (monitored by TLC). Then, hydrazine hydrate (80 wt%, 6 eq) was added to the reaction vessel. After completion of the reduction process, the mixture was filtered and washed with water. The organic layer was extracted with ethyl acetate (3 × 15 mL) and dried over MgSO₄. Then the organic solution was concentrated and purified by column chromatography to obtain the final product.

3 Results and Discussion

3.1 Characterization of Ni₇–Pd₃@BIHPS

The FT-IR spectra of Luffa, BIHPS, and Ni₇-Pd₃@BIHPS are presented in Fig. 1. For Luffa, the peaks at 3421 and 1645 cm⁻¹ are related to the surface OH groups and absorbed water. Also, the peaks at 2921 and 1740 cm⁻¹ are attributed to the C-H and C=O stretching, respectively. The peaks at 1502, 1433 and 1347 cm^{-1} correspond to the CH, CH₃ and CH₂ groups and the peak at 1058 cm⁻¹ corresponds to the C–O–C stretching [39]. For BIHPS, the observed peaks at 3464 and 1645 cm⁻¹ are attributed to the stretching and bending vibration of O-H group of adsorbed water on the surface of BIHPS like Luffa. The peaks at 1085, 801 and 471 cm⁻¹ are related to the Si-O-Si and Si-OH stretching, which confirms the formation of condensed silica support [40]. Moreover, other peaks related to luffa cannot be seen in BIHPS, which means that luffa template is successfully removed. The FT-IR spectrum of Ni₇-Pd₃@

BIHPS presented the same bonds of pristine BIHPS only with decreasing the intensity of O–H peaks at 3430 cm^{-1} , which can be related to the grafting of Ni–Pd alloy NPs onto the BIHPS surface [41].

The N₂ adsorption-desorption isotherms and BJH pore size distribution plots of BIHPS and Ni₇-Pd₃@BIHPS are depicted in Fig. 2. Also, the porosity parameters and specific surface area for these samples are listed in Table 1. As shown in Fig. 2a, BIHPS exhibited type IV isotherms with hysteresis in the p/p_0 at 0.4–1.0, which is related to the mesopores structure [42]. According to Table 1, the specific surface area, pore volume and pore size of BIHPS are 336 m² g⁻¹, 0.77 cm³ g⁻¹ and 9.1 nm, respectively. In spite of the mesoporous structure, MP-plot and t-plot showed the existence of microporous in the structure of BIHPS (Table 1). These results confirmed the formation of hierarchical microporous-mesoporous silica with a high surface area. As it can be seen in Fig. 2c, Ni₇-Pd₃@BIHPS revealed type IV isotherms, which is related to the mesopores structure like BIHPS. In comparison with BIHPS, the specific surface area, pore volume and pore size of Ni₇-Pd₃@ BIHPS are decreased to 80 m² g⁻¹, 0.12 cm³ g⁻¹, and 8.1 nm, respectively, which are confirmed that Ni–Pd alloy NPs are dispersed on the outer surface and inside the pores of BIHPS [43]. Also, the MP-plot and t-plot of Ni₇-Pd₃@ BIHPS showed the presence of microporous structures after the incorporation of Ni-Pd NPs (Table 1).

The XRD of Pd@BIHPS, Ni@BIHPS, Ni7-Pd3@BIHPS and BIHPS were shown in Fig. 3. The XRD of Pd@BIHPS and Ni@BIHPS are used for comparison. For all samples, a broad peak has appeared at 21.4°, which corresponds to the amorphous silica. For Pd@BIHPS, the peaks at 20 values of 39.9° , 46.8° and 68.2° were related to the (111), (200) and (220) diffraction planes of fcc crystalline structure of Pd. The XRD pattern of Ni@BIHPS didn't show any clear peaks for Ni, which can be related to the small size and amorphous nature of Ni NPs. XRD pattern of Ni₇-Pd₃@ BIHPS shows a slight shift in (111) diffraction peak of Pd towards higher angel (40.6°) and also the intensity of this peak decreased as compared to Pd@BIHPS. These results indicate the incorporation of Ni and Pd in the same lattice and also, the formation of NiPd alloy [2]. The average size of Ni-Pd alloy NPs is 8.04 nm, which is calculated from the (111) diffraction peak of Ni₇-Pd₃@BIHPS using Scherrer's equation [44].



Fig.1 FT-IR spectra of (a) Luffa, (b) BIHPS and (c) Ni_7 -Pd₃@ BIHPS

The FESEM images of Luffa are presented in Fig. S2, which show the fibrous structure with hollow channels for Luffa. It is notable that these hollow channels play a specific role in the efficient loading of metal NPs. The FESEM images of BIHPS, and Ni7-Pd3@BIHPS are presented in Fig. 4. The images of BIHPS exhibit the vascular structure, which is in agreement with the luffa structure and this also confirms that the replication process has been carried out successfully using sol-gel method (Fig. 4a, b). The images of Ni₇-Pd₃@BIHPS show that the cylindrical structure of BIHPS is well reserved after the incorporation of Ni-Pd NPs. Also, the surface of Ni₇-Pd₃@BIHPS seems to be rough compared with BIHPS (Fig. 4c, d). Furthermore, the FESEM-mapping of Ni7-Pd3@BIHPS was carried out to reveal the dispersion of Pd and Ni NPs on the surface (Fig. 4e). These images show that Ni-Pd NPs dispersed uniformly on the surface of BIHPS in the randomly selected area, which confirms the formation of Ni-Pd alloy NPs. Also, the FESEM–EDX analyze of Ni₇–Pd₃@BIHPS was carried out to identify the elemental composition for the same selected area of surface (Fig. 4f). The outcomes confirmed the distribution of Ni, Pd, Si and O elements on the surface of this catalyst. Based on the EDX results, the Ni/





Fig. 2 a N_2 adsorption-desorption isotherms of BIHPS, b BJH pore size of BIHPS, c N_2 adsorption-desorption isotherms of Ni_7 -Pd₃@ BIHPS and d BJH pore size of Ni_7 -Pd₃@BIHPS

Pd atomic ratio was calculated 0.46, which is lower than the ICP-AES value of 2.19. This difference can be attributed to the main distribution of Pd on the outer surface of Ni_7 -Pd₃@ BIHPS. Also, it should be mentioned that EDX analysis is a qualitative method not a quantitative one. Therefore, EDX analysis is not a reliable method to determine the percent of elements and we trust in ICP results.



Fig. 3 XRD patterns of (*a*) BIHPS, (*b*) Ni₇–Pd₃@BIHPS, (*c*) Ni@ BIHPS and (*d*) Pd@BIHPS

TEM images of Ni₇–Pd₃@BIHPS represented in Fig. 5a. As it can be seen, Ni–Pd NPs have appeared as black dots, and also it is clear that these NPs have been well-dispersed onto the BIHPS, but in some where low agglomeration is observed. The HRTEM images displayed the lactic distance of 0.241 nm for alloyed Ni–Pd, which corresponding to the fcc crystalline structure (Fig. 5b, c). Also, the histogram of Ni–Pd size distribution is presented in Fig. 5d, which is exhibited that the average size distribution of NPs is 7–9 nm in Ni₇–Pd₃@BIHPS. This average size is in agreement with the obtained size from XRD.

The DRS UV-vis spectra of Ni₇²⁺–Pd₃²⁺@BIHPS, Ni₇–Pd₃@BIHPS, and BIHPS are presented in Fig. S3. According to the results reported in the literature, the peaks of Pd²⁺ and Ni²⁺ appear at 312, 392 nm and 368, 576 nm, respectively [45]. In Ni₇²⁺–Pd₃²⁺@BIHPS, the peaks of Ni²⁺ and Pd²⁺ were overlapped with the BIHPS peaks and showed the broad peak from 311 to 398 nm, and only the peak of Ni²⁺ at 576 nm has been obviously appeared. As shown in Fig. S2, the Ni₇–Pd₃@BIHPS and BIHPS spectra are almost

Table 1 Physicochemical parameters of BIHPS and Ni_7 -Pd₃@BIHPS obtained from N_2 adsorption-desorption

Sample	$\frac{S_{mesopore}}{(m^2 g^{-1})}^a$	V_{mesopore}^{a} (cm ³ g ⁻¹)	D _{mesopore} ^b (nm)	$\frac{S_{micropore}}{(m^2 g^{-1})}^c$	$V_{\text{micropore}}^{c}$ (cm ³ g ⁻¹)	D _{micropore} ^c (nm)
BIHPS	336	0.77	9.1	419	0.19	2
Ni7-Pd3@BIHPS	80	0.12	8.1	59	0.05	2

^aCalculated by BET method

^bMean pore diameter determined using BJH method

^cCalculated by MP-plot method

Fig. 4 a, b FESEM images of BIHPS, **c, d** FESEM images of Ni₇-Pd₃@BIHPS, **e** FESEMmapping of Ni₇-Pd₃@BIHPS and **f** FESEM-EDX analyze of Ni₇-Pd₃@BIHPS





Fig. 5 a TEM images of Ni_{7} -Pd₃@BIHPS, **b**, **c** HRTEM images of Ni_{7} -Pd₃@BIHPS and **d** corresponding histogram of size distribution of nanoparticles



identical and the absence of the peak at 576 nm in Ni_7 -Pd₃@ BIHPS indicates that Ni^{2+} and Pd²⁺ species are reduced to Ni and Pd NPs.

X-ray photoelectron spectroscopy (XPS) was carried out for surface compositional studies of Ni7-Pd3@BIHPS. The wide-survey XPS spectra of Ni7-Pd3@BIHPS displayed peaks of silicon, carbon, oxygen, palladium, and nickel (Fig. S4). The high resolution spectra of Si and O are depicted in Figs. S5 and S6, respectively. The peak of Si 2p is revealed at 103.34 eV, which confirms the formation of SiO₂ (Fig. S5) [46]. Meanwhile, the O 1S peak at 532.95 was originated because of the Si-O bond and a small peak at 530.95 eV is related to O^{2-} , which can be originated from the bonding of the metal oxides (Fig. S6) [47]. The high resolution spectra of Pd and Ni are presented in Fig. 6a, b, respectively. As seen in Fig. 6a, the high resolution spectra of Pd exhibit four peaks at 335.31, 336.33, 340.58 and 341.48 eV. The peaks at 335.31 and 340.58 eV were corresponded to 3d_{5/2} and $3d_{3/2}$ of metallic Pd, while the binding energies at 336.33

and 341.48 eV related to 3d_{5/2} and 3d_{3/2} of Pd²⁺, respectively [8, 48]. These results indicate that the reduction of Pd^{2+} has been successfully done. Also, the binding energy of Pd 3d in Ni₇-Pd₃@BIHPS appeared in higher binding energy than the standard Pd, which can be attributed to the existence of Ni with high d-bond vacancies in the Pd lattice and also the electron-withdrawing effects from Pd in Ni-Pd alloy [6, 44]. As shown in Fig. 6b, the high resolution spectra of Ni exhibited a broad peak at 853.78 eV, which can be assigned to metallic Ni. It is notable that this peak is depicted in high binding energy compared to standard binding energy. Also, the peaks at 856.42 and 874.38 eV were ascribed to Ni²⁺ $2p_{3/2}$ and Ni²⁺ $2p_{1/2}$, respectively [6]. Furthermore, $2p_{3/2}$ satellite and $2p_{1/2}$ satellite of Ni²⁺ appeared at 862.28, 862.28 and 879.88 eV [49]. It is notable that the appearance of Ni^{2+} and Pd²⁺ in XPS spectrum is due to the air oxidation of subsurface Ni and Pd atoms during the analyze [50].

3.2 Catalytic Activity

After fabrication and characterization of BIHPS, it was used as support for Ni–Pd alloy NPs. The supported Ni–Pd



Fig. 6 a High resolution XPS spectra of Pd in Ni_7 –Pd₃@BIHPS and b high resolution XPS spectra of Ni in Ni_7 –Pd₃@BIHPS

was used as a promoter in the synthesis of aminobiphenyls from the one-pot Suzuki coupling-nitro reduction reaction. For optimization of the reaction conditions, we selected the model reaction involving 1-iodo-3-nitrobenzene and phenylboronic acid for surveying the effect of different parameters to find the optimum conditions (Table 2).

Without the use of the catalyst, no product was observed in H₂O/DMF mixture solvent and K₂CO₃ base at 100 °C (Table 2, entry 1). Also, the reaction in the presence of BIHPS without NiPd NPs, no product was observed (Table 2, entry 2). But, with use of Pd@BIHPS, 3-aminobiphenyl was isolated about 48% (Table 2, entry 3). To improve the catalytic activity, we investigated the effect of Ni on Pd with the different molar ratio (Table 2, entry 4–6). With the use of Ni@BIHPS without Pd, the corresponded product was gained about 5% (Table 2, entry 7). The best yield of the product was gained when we used Ni–Pd with 7:3 molar ratio (Table 2, entry 4). The better catalytic activity of Ni-Pd alloy than the Pd may be related to the synergistic effects of the individual components. Also, with increasing the total amount of metals from 0.02 to 0.03 mmol, 3-aminobiphenyl was isolated approximately 92% (Table 2, entry 8). Also, the effect of different solvents was investigated in this reaction (Table 2, entry 8–13). These result confirmed that we gained the high yield of the product by using H₂O/DMF (2:1). Among various bases, K₂CO₃ as a weak base showed the best result in this protocol (Table 2, entry 8). With decreasing the temperature to 80 °C the yield of products remained constant, but further decreasing of temperature to 70 °C lead to decrease in yield (Table 2, entry 18–19). Therefore, the best temperature was chosen 80 °C. For the reduction of 3-nitrobiphenyl to 3-aminobiphenyl, we used 6 eq of hydrazine hydrate as a hydrogen source. With decreasing the amount of hydrazine hydrate from 6 to 4 eq, the yield of the product was decreased (Table 2, entry 20).

To optimize the amount of $Ni_7-Pd_3@BIHPS$, we changed the amount of the catalyst from 30 to 20 mg and 40 mg in the model reaction under optimal conditions (Fig. 7). The results showed that decreasing of the catalyst amount caused to 53% product in 180 min, and the high amount of catalyst had no any considerable effect on the yield and time. Based on these results, we selected 30 mg of $Ni_7-Pd_3@BIHPS$ as the optimal amount of the catalyst.

Under the optimal conditions, a variety of aryl boronic acid and aryl halides with nitro groups were reacted (Table 3). It was seen that the reaction of the phenylboronic acid with 1-iodo-3-nitrobenzene is faster than 1-bromo-3-nitrobenzene (Table 3, entry 1–2). Also, reaction with 1-chloro-3-nitrobenzene gave the product in 54% yield after 12 h (Table 3, entry 3). In general, phenylboronic acid with electron-donating groups afforded high yields of the products at slightly lower time compared to electron-withdrawing groups. As shown in Table 3, entry 6, 1-iodo-2-methyl-4-nitrobenzene as a sterically hindered substrate afforded the corresponding product in 82% yields at 5.5 h. Furthermore, 2-chloropyridine as a heteroaryl halide reacted with 3-nitrophenylboronic acid and produced the desired amine in 78% at 9 h (Table 3, entry 13).

Scheme 2 illustrates the possible mechanism of the reaction. At first, Pd-complex (**A**) generates via the oxidative addition of aryl hailed to the Pd (0). Then, during transmetalation between **A** and activated phenylboronic acid by K_2CO_3 , organopalladium (**B**) obtains. Reductive elimination of **B** gives the final coupled product (**C**) and regenerates the catalyst for the next catalytic cycle [34]. For the reduction step, hydrazine hydrate was decomposed in the presence of Ni₇-Pd₃@BIHPS, which produced hydrogen and nitrogen. Then, nitrobiphenyls was converted to aminobiphenyls using the produced hydrogen [51]. Table 2 Optimization conditions for Ni-Pd@BIHPS catalyzed one-pot Suzuki-Miyaura cross coupling-nitro reduction between 1-iodo-3-nitrobenzene and phenylboronic acid



Entry	Ni:Pd molar ratio in 0.1 g BIHPS	Total amount of metals (mmol) in 0.1 g BIHPS	Solvent	Base	T (°C)	N ₂ H ₄ ·H ₂ O (equiv.)	Yield (%) ^a
1	None	None	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	0	0
2	None ^b	None	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	0	0
3	0:10	0.02	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	6	48
4	7:3	0.02	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	6	68
5	9:1	0.02	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	6	35
6	8:2	0.02	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	6	50
7	10:0	0.02	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	6	5
8	7:3	0.03	H ₂ O/DMF (2:1)	K ₂ CO ₃	100	6	92
9	7:3	0.03	H ₂ O	K ₂ CO ₃	100	6	51
10	7:3	0.03	EtOH	K ₂ CO ₃	100	6	50
11	7:3	0.03	H ₂ O/EtOH (2:1)	K ₂ CO ₃	100	6	75
12	7:3	0.03	Dioxane	K ₂ CO ₃	100	6	20
13	7:3	0.03	DMF	K ₂ CO ₃	100	6	58
14	7:3	0.03	H ₂ O/DMF (2:1)	Et ₃ N	100	6	20
15	7:3	0.03	H ₂ O/DMF (2:1)	KOH	100	6	42
16	7:3	0.03	H ₂ O/DMF (2:1)	Cs ₂ CO ₃	100	6	50
17	7:3	0.03	H ₂ O/DMF (2:1)	NaHCO ₃	100	6	46
18	7:3	0.03	H ₂ O/DMF (2:1)	K ₂ CO ₃	80	6	91
19	7:3	0.03	H ₂ O/DMF (2:1)	K ₂ CO ₃	70	6	80
20	7:3	0.03	H ₂ O/DMF (2:1)	K ₂ CO ₃	80	4	75

Reaction conditions: 1-iodo-3-nitrobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), solvent (3.0 mL), base (2.0 mmol), Ni–Pd@BIHPS (30 mg) and time (120 min)

^aIsolated yields

^bBIHPS without NiPd NPs

In order to prove this mechanism, the coupling reaction between 1-iodo-2-methyl-4-nitrobenzene and phenyl boronic acid was carried out. Then, before the adding of hydrazine hydrate, the product was isolated and studied by ¹HNMR. Also, the ¹HNMR of the product gained from tandem cross coupling-nitro reduction was also reported in below. Comparison of these results proved the rationality of this mechanism.

2-Methyl-4-nitro-1,1'-biphenyl: ¹HNMR (300 MHz, CDCl3, ppm): 8.15 (s, 1H, Ar–H), 8.08 (d, 1H, *J*=9 Hz, Ar–H), 7.54–7.41 (m, 3H, Ar–H), 7.37 (d, 1H, *J*=9 Hz, Ar–H), 7.32–7.28 (m, 2H, Ar–H), 2.36 (s, 3H, CH3).

2-Methyl-[1,1'-biphenyl]-4-amine: ¹HNMR (300 MHz, CDCl3, ppm): 7.40–7.35 (m, 2H, Ar–H), 7.31–7.23 (m, 3H, Ar–H), 7.05 (d, 1H, *J*=9 Hz, Ar–H), 6.64 (d, 2H, *J*=9 Hz, Ar–H), 3.80 (s, 2H, NH₂), 2.31 (s, 3H, CH3).



Fig. 7 Optimization of catalyst loading [reaction condition: 1-iodo-3-nitrobenzene (1.0 mmol), phenyl boronic acid (1.1 mmol), K_2CO_3 (2 mmol) in H_2O/DMF (2:1) at 80 °C and catalyst (Ni_7 – $Pd_{3@}BIHPS$)]

 Table 3
 Ni7-Pd3@BIHPS-catalyzed one-pot Suzuki-Miyaura cross coupling nitro reduction of different aryl halides and phenyl boronic acids



Entry	Aryl halides	Arylboronic acid	Product	Time (h)	Yield (%) ^a
1	O ₂ N	(HO) ₂ B	H ₂ N	2	91
2	O ₂ N Br	(HO) ₂ B	H ₂ N	5	85
3	O ₂ N CI	(HO) ₂ B	H ₂ N	12	54
4	O ₂ NI	(HO) ₂ B	H ₂ N	2.5	90
5	O ₂ NI	(HO) ₂ B	H ₂ N	1.5	90
6	O ₂ N-I	(HO) ₂ B	H ₂ N-	5.5	82
7	O ₂ N	(HO) ₂ B	H ₂ N	1.5	92
8	O ₂ N-Br	(HO) ₂ B	H ₂ N	6	80
9		(HO) ₂ B	NH ₂	3.5	87
10		(HO) ₂ B	NH ₂	3.5	80
11		(HO) ₂ B		3	84
12	Br	(HO) ₂ B	NH ₂	6.5	82
13		(HO) ₂ B		9	78

Table 3 (continued)

Reaction conditions: phenylboronic acid (1.1 mmol), aryl halide (1.0 mmol), H₂O/DMF (2:1), K₂CO₃ (2.0 mmol), N₂H₄.H₂O (6 eq), Ni₇–Pd₃@BIHPS (30 mg) at 80 °C ^aIsolated yields



In order to determine the heterogeneity nature of the catalyst, two separate coupling reactions were carried out between 1-iodo-3-nitrobenzene and phenylboronic acid in the presence of Ni_7 -Pd₃@BIHPS under optimal condition. The first reaction was stopped after 10 min and filtered, then the reaction was continued with the filtrated for an extra 3 h,

then the coupling product was isolated. The second reaction was also stopped after 10 min and the product was also isolated. The outcomes revealed that in both reactions, the cross-coupling products were obtained in the same yields (58%). The results of these two experiments confirmed that the reactions proceed on the heterogeneous surface of



Fig. 8 Reusability of catalyst (reaction condition: 1-iodo-3-nitrobenzene (1.0 mmol), phenyl boronic acid (1.1 mmol) and K_2CO_3 (2 mmol) in H_2O/DMF (2:1) at 80 °C and N_2H_4 · H_2O 80% (6 eq))

Ni₇–Pd₃@BIHPS [52]. Based on the obtained results from the heterogeneity experiment, we decided to explore the reusability of the catalyst (Fig. 8). For this propose, after completion of the reaction between 1-iodo-3-nitrobenzene and phenylboronic acid followed by reduction, the catalyst was separated by centrifugation and washed with water (15 mL) and acetone (10 mL), then dried at 80 °C for 3 h and reused for next cycle. It was notable that Ni₇-Pd₃@BIHPS was reused for six times without significant decreases in its catalytic activity. Also, ICP-AES estimated 0.0654 mmol g⁻¹ Pd and 0.1434 mmol g^{-1} Ni content of used catalyst after five runs, which exhibited only 0.9 and 1.1% leaching for Pd and Ni, respectively (Table S3). The decline in recycle activity of the catalyst probably could be related to the very low leaching of Pd–Ni NPs from support (0.9% Pd, 1.1% Ni) or aggregations of nanoparticles on the surface [9].

XRD pattern of the reused catalyst exhibited the existence of Ni–Pd alloyed NPs on the surface of BIHPS after fifth run (Fig. S7). Moreover, the FESEM images of reused catalyst showed that the structure of the fresh catalyst is preserved even after fifth run (Fig. S8). Also, FESEM-mapping and FESEM-EDX of the catalyst after the fifth times showed the good dispersion of Pd and Ni NPs on the surface (Fig. S9a, b).

To illustrate the efficiency of our synthesized support (BIHPS) in the synthesis of 4-aminobiphenyl, Table 4 compares our result with some carbon and silica beds.

4 Conclusion

In summary, Luffa sponge was used as an inexpensive biotemplate for the synthesis of a new bio-inspired hierarchical porous silica support (BIHPS). BIHPS exhibited high potential to immobilizing of Ni–Pd alloy NPs. The synergistic effect between Ni and Pd in Ni₇–Pd₃@BIHPS revealed the excellent catalytic activity in the one-pot Suzuki–Miyaura coupling-nitro reduction reaction, compared to each metal alone. This catalyst also showed high stability after six runs. Use of low amount of Pd, short reaction times, high yields of the products, heterogeneous nature of the reaction, reusability of the catalyst are some unique features of this catalyst. Scientifically, the synthesized support can also be used for immobilizing of other alloy NPs such as Au–Pd, Pd–Ag due to owing the high surface area and hierarchical structure.

Acknowledgements The authors would like to acknowledge financial support by Kharazmi University.

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Entry	Catalyst	Pd (mol%)	Ni (mol%)	Temperature (°C)	Time (h)	Yield ^a (%) [References]
1	Ni7-Pd3@BIHPS	0.19	0.43	80	2.5	90 [This work]
2	Ni7-Pd3@Silicab	0.19	0.43	80	10	56 ^c
3	Ni7-Pd3@MMTd	0.19	0.43	80	5.5	62 ^c
4	Pd cNPs/C@Fe ₃ O ₄	0.73	-	70	3	91 [33]

Table 4 Comparison of the results obtained from the synthesis of 4-aminobiphenyl via the reaction between 1-iodo-4-nitrobenzene and phe-nylboronic acid in the presence of Ni_7 -Pd₃@BIHPS with those obtained using other heterogeneous catalysts

^aIsolated yield

^bCommercially available silica

^cSynthesized = in our group for comparison

^dNa-montmorillonite clay

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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