FULL PAPER



Nanopalladium on polyethylenimine–grafted starch: An efficient and ecofriendly heterogeneous catalyst for Suzuki–Miyaura coupling and transfer hydrogenation reactions

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Shanghai Commission of Science and Technology, Grant/Award Number: 08431901800 Functionalized natural polysaccharides are attractive supports for colloidal metal nanocatalysts due to their abundance, cheapness, biocompatibility and biodegradability. In this study, isocyanate–functionalized starch was prepared by treating with diisocyanate. Polyethylenimine grafted onto starch *via* the formation of urea linker. The palladium nanoparticles deposited starch PEIS@Pd(0) was obtained through a chelating–*in situ* reduction procedure. Characterization of these materials was done using Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, X–ray diffraction, and inductive coupled plasma atomic emission spectrometry. The catalytic activity of PEIS@Pd(0) was then tested in two series of model reactions: Suzuki–Miyaura coupling and transfer hydrogenation. The catalyst could be recovered by simple filtration and was reused for five times without significant loss of catalytic activity, which confirmed the good stability of the catalyst.

KEYWORDS

catalyst, palladium nanoparticles, polyethylenimine, Suzuki-Miyaura coupling, transfer hydrogenation

1 | **INTRODUCTION**

Despite the excellent activity and selectivity of homogeneous catalysts, they have inherent drawbacks in catalyst separation and recycling. In contrast, heterogeneous catalysts are much affordable for industrial application.^[1] Nanometer–sized colloidal metal catalysts, sometimes termed semi–heterogeneous or quasi–homogeneous catalysts, have received increasing attention because they often offer higher catalytic efficiency than larger size materials, because of their large surface–to–volume ratio.^[2] However, two technical issues restrict their wide applications. First, the separation and recovery of such catalytic nanoparticles in their isolated form is very challenging due to their small sizes. Residual nanocatalysts are generally considered very undesirable because of their potential harmful impact on the environment. Immobilization of nano–sized metal catalysts onto

solid substrates can stabilize the catalysts and allow their recycled uses. $\ensuremath{^{[3]}}$

The application of solid–supported noble metal nanocatalysts, particularly Pd(0) clusters, has increased dramatically in recent years. Among various solid supports such as functionalized oxide,^[4] charcoal,^[5] zeolite,^[6] polymer,^[7] and metal–organic framework,^[8] ecofriendly natural polysaccharides (e.g. starch and cellulose) are attractive ones due to their abundance, biocompatibility and biodegradability.^[9] For example, carboxymethylcellulose–supported palladium nanoparticles generated *in situ* from palladium(II) carboxymethylcellulose was found to be an efficient and reusable catalyst for Heck–Matsuda and Suzuki–Miyaura couplings.^[10] Palladium and Fe₃O₄ nanoparticles could be deposited onto N–(2–aminoethyl)acetamide functionalized cellulose afforded a reusable catalyst in the oxidation reaction of ethylbenzene.^[11]

Functional polymers provide stabilization for metal nanoparticles through the framework or by binding weakly to the nanoparticle surface through heteroatoms. Polyethylenimine (PEI) is a branched, water-soluble polymer used for a wide variety of applications. As a chelating agent, PEI plays the role of efficient stabilizer during the preparation^[12] or assembly^[13] of noble metal nanoparticles. PEI modified solids are satisfactory supports of noble metal nanocatalysts. Gold nanoparticles immobilized on PEI modified polyacrylonitrile fiber is a highly efficient and recyclable heterogeneous catalyst for the reduction of 4-nitrophenol by NaBH₄.^[14]

PEI can also be grafted onto natural polysaccharides through chemical modification. PEI–grafted starch,^[15] cellulose^[16] and chitosan^[17] were applied for the removal of heavy metal ions from aqueous solutions. The biocompatible backbone of polysaccharides is favorable in biological research. Recently, polysaccharides grafted with PEI were introduced as gene delivery platform^[18] and vehicles for drug delivery.^[19] To the best of our knowledge, however, the PEI–grafted polysaccharide as functional support of noble metal nanocatalysts has not yet been investigated.

Herein, we report the design and preparation of PEIgrafted starch supported palladium nanoparticles with the aim to develop an efficient catalytic system that promotes various reactions. The functional support was obtained by grafting polyethylenimine onto isocyanate-functionalized starch. In comparison with traditional epoxide ring opening amination route, this activation method was demonstrated to be much efficient. The catalyst was synthesized through a chelating-in situ reduction method to form monodispersed Pd NPs with an average diameter of ~8 nm on the surface of the PEI grafted starch. The catalytic activity of as-synthesized PEIS@Pd(0) was evaluated in two model reactions: (1) Suzuki-Miyaura coupling reaction between substituted bromobenzenes and arylboronic acids, and (2) transfer hydrogenation of carbonyl compounds and chalcones with HCOONH₄ as hydrogen donor. The catalyst can be recovered and recycled for at least five times without significant loss of catalytic activity.

2 | RESULTS AND DISCUSSION

2.1 | Surface activation and grafting

The processes of surface activation, polyethylenimine– grafting, and depositon of palladium nanoparticles were illustrated in Scheme 1. Polyethyleneimine (PEI) is a polymer without uniform repeat units. It contains linear regions and branched regions with primary amino functions as terminal units and secondary amino functions as linear units. The dendritic units consist of tertiary amines (Scheme 1A).^[20] This fact made it an efficient polymeric ligand for the chelation of metal cations as well as stabilization of metal



SCHEME 1 Preparation of polyethylenimine–grafted starch and depositon of palladium nanoparticles

nanoparticles. Starch has great number of hydroxyl groups on the surface capable of chemical modification. Initially, the starch granules were activated by treating with *p*-phenylene diisocyanate (1 equiv. per glucose unit) in anhydrous acetonitrile for 12 hours at room temperature. Symmetric diisocyanate was anchored on the surface of starch by forming carbamate linkage, with another isocyanate group remained as a reaction site for further decoration. The reactive support thus obtained was grafted with polyethyleneimine ($M_w \approx 600$, Aldrich) to afford PEI grafted starch (denoted as PEIS).

Routinely, polyethylenimine–grafted polysaccharides were prepared by treating PEI with epoxy–functionalized polysaccharides (epoxide ring opening amination route). The epoxide moiety is a strained but apparently stable three membered ring. Epoxide ring opening amination often needs catalysts, elevated temperatures or long reaction times (e.g. 60°C, 12h^[21]). Hence, microwave irradiation has recently been reported to accelerate the grafting of PEI on epoxy–functionalized cellulose fiber.^[22] In the present work, isocyanate–functionalized starch was employed as a much efficient reactive support in comparison with epoxy–functionalized one. In our investigation, a short reaction time and mild condition (room temperature, 3h) were chosen for grafting procedure. This success depends on the excellent reactivity of isocyanate group with amino groups on PEI.

Surface modification was confirmed by Fourier transform infrared spectroscopy. The appearance of absorption band at 2280 cm^{-1} is attributed to the isocyanate groups stretching vibration, while the absorption peaks at 1639 and 1561 cm⁻¹

is related to C=O stretching vibration and N–H bending vibration, respectively (Figure 1, b). These facts proved that the starch was funtionalized by diisocyanate through a carbamate linkage. The characteristic peak of isocyanate disappeared after the isocyanate–functionalized starch was treated with PEI (Figure 1, b and c), indicating the complete consumption of isocyanate groups during grafting. The loading of amino groups on PEIS was determined as 7.5 mmol/g by acid–base titration analysis. According to the result of nitrogen content determined by elemental analysis, amine group loading was calculated as 8.3 mmol/g. This difference might be partly attributed to the existence of nitrogen in the linkages.

The surface morphology of unmodified starch and PEI grafted starch were observed through SEM images as shown in Figure 2. It shows that the starch granules present regular surface morphology. The grafting of PEI had no significant effect on the surface morphology, indicating the structure of starch granules had not been destroyed during the chemical modification.

2.2 | Depositon of palladium nanoparticles

Pd(0) loaded PEIS was obtained through a chelating–*in situ* reduction procedure. As-prepared PEIS was then tested as a chelating support of palladium catalyst since Pd(II) could be bound readily by coordination to the amine groups. Pd(II) loaded PEIS was firstly prepared by exposing PEIS to PdCl₂ solution, followed by washing with ethanol to remove unbinding Pd(II) ions. In a one–pot *in situ* reduction procedure, above–mentioned suspension of Pd(II) loaded PEIS could be transformed to PEIS@Pd(0) through *in situ* reduction the color of catalyst changed rapidly from yellow–gray to black due to the formation of black Pd(0) nanoparticles.

X-ray diffraction (XRD) patterns of blank PEIS support, Pd(II) loaded PEIS and PEIS@Pd(0) were shown in Figure 3. A broad reflection $(2\theta=10-40^{\circ})$ is observed in the XRD



FIGURE 1 FTIR spectra of (a) unmodified starch (b) isocyanatefunctionalized starch and (c) PEI grafted starch





FIGURE 2 SEM images of (a) unmodified starch (b) PEIS



FIGURE 3 XRD patterns of (a) blank PEIS support, (b) Pd(II) loaded PEIS and (c) PEIS@Pd(0). Inserts illustrate the digital photographs of corresponding samples

patterns of blank PEIS support and Pd(II) loaded PEIS (Figure 3, a and b, respectively), which is attributed to the reflection of amorphous matrix. The pattern of PEIS@Pd recycled after hydrogenation reaction exhibited characteristic diffused peaks around 40°, 46°, and 68°, which could be

assigned to (111), (200) and (220) reflections of the face centered cubic (fcc) structure corresponding to metallic palladium,^[23] indicating that the Pd was deposited on the support as nanocrystals. It should be mentioned that certain reflection peaks in low-intensity could be identified at $2\theta = 40^{\circ}$ and 46° , implying that small amount of metallic Pd exists in the sample of Pd(II) loaded PEIS (Figure 3, b). This observation might to be ascribed to the weak reductive activity of starch. ^[24]

Furthermore, the formation of Pd nanoparticles was confirmed by transmission electron microscopy (TEM) as presented in Figure 4. No clearly visible nanoparticles could be observed on Pd(II) loaded PEIS (Figure 4, A). In contrast, TEM image of PEIS@Pd(0) recovered after hydrogenation displayed the well dispersed nature of the Pd NPs situated on the external surface of the support (Figure 4, B). The marked rectangle is magnified in Figure 4C, shows that the well monodispersed Pd NPs on PEI grafted starch were of nearly spherical shape, with an average diameter of 4.3 nm as can be seen in the embedded histogram. The average particle size of the Pd NPs was further estimated by the peak width of the (111) Bragg reflection using Scherrer's equation: $D = K\lambda/\beta \cos\theta$, where β is the half-peak width of the corresponding peak, θ is the diffraction angle, λ is the wavelength of the Cu K_{α} radiation (0.154178 nm), and K is a constant of value 0.89. The average diameter was calculated to be 5.5 nm, which was consistent with the results from the TEM image. The percentage of palladium content in the PEIS@Pd(0) catalysts was determined by chemical analysis using inductive coupled plasma atomic emission spectrometry (ICP-AES). The accurate content of Pd on PEIS@Pd(0) was determined to be 9.6% wt, which is equal to 0.90 mmol/g.

2.3 | Suzuki–Miyaura coupling reaction

The palladium–catalyzed Suzuki–Miyaura cross–coupling reaction of aryl halides with arylboronic acids is one of the most powerful and versatile methods for the synthesis of symmetric and asymmetric biaryls.^[25] Over the past decades, this reaction has achieved great progress and been applied extensively in material science and fine chemicals and pharmaceutical industries.^[26] On the other hand, the catalytic activities of palladium catalysts are commonly tested using Suzuki–Miyaura coupling reaction.

The coupling of bromobenzene and phenylboronic acid was chosen as a model for studying the effects of different solvents and bases. Only ethanol, water and their mixture were chosen as solvents due to environmental concerns. The amount of PEIS@Pd(0) was initially fixed as 2mol%(calculated based on palladium content) with K₂CO₃ as a base (Table 1, Entries 1–5). The screening experiment reveals that the reaction was performed in water the yield was very low (38% after 4 h). The mixtures of EtOH/H₂O are better reaction media than pure ethanol. The ratio of EtOH/H₂O also influenced the efficiency and EtOH:H₂O=1:1(ν/ν) was the best choice (Table 1, Entries 3–5). The advantage of the mixed solvent might to be attributed to the good solubility of the organic reactants and the inorganic base.

After fixing a suitable solvent, the reaction was repeated using different bases (Table 1, Entries 6–10). Among the bases, K_2CO_3 was proved to be the best one. K_3PO_4 and Na_2CO_3 were also effective. Unfortunately, NaHCO₃ and an organic base, triethylamine, did not give ideal reactivity under the same reaction conditions (Table 1, Entries 9 and 10). The influence of the amounts of catalyst was also investigated. Catalytic amount (2mol%) of Pd was sufficient for a satisfactory result, while an increase in the proportion to 3mol% produced comparable yields. Smaller amounts of Pd (1mol%) resulted in an inferior yield (Table 1, Entries 11 and 12).

With the optimized reaction conditions in hand, the substrate scope of PEIS@Pd(0) in Suzuki–Miyaura coupling reaction was investigated, for which a range of phenyl bromides and aryl iodides were coupled with various phenylboronic acids (Scheme 2). In general, good to excellent yields (87–92%) of corresponding biphenyl compounds were obtained after 2–4 h with 2 mol% palladium loading (Table 2). Arylboronic acid bearing strong electron–donating groups need a relatively longer time to produce a good yield, and the steric hindrance effect might have a certain impact on the reaction rate (Table 2, Entry 12).

The recyclability of PEIS@Pd(0) catalyst was further investigated because the good recyclability of the heterogeneous catalyst is an important issue for practical applications. The recyclability was assessed in model reaction under optimized reaction conditions. On completion of the reaction, the catalyst was recovered from the reaction mixture by filtration, washed several times with water and ethanol, and dried in air. The catalyst could be reused for at least five cycles without a significant loss of yield and catalytic activity (Table 2, Entries 1-6). The recyclability of the catalyst can be attributed to the efficient stabilization of the Pd nanoparticles. The TEM image of PEIS@Pd(0) after consecutive six runs of Suzuki-Miyaura coupling reaction shows that there is no agglomeration of Pd nanoparticles (Figure 4D). Furthermore, the filtrate was subjected to ICP-AES to check the possible leaching of palladium from PEIS@Pd(0) with the satisfactory result indicating the absence of leaching from the catalyst. Namely, the catalyst was very stable under the reaction condition.

Finally, we compared the results achieved in this work with those reported elsewhere over many supported catalysts. Taking phenyl bromide reaction with phenylboronic acid as an example, the results are listed in Table 3. The turnover number (TON=mol of product/mol of catalyst) and turnover frequency (TOF =TON/time (h)) were calculated on the basis



FIGURE 4 TEM images of (a) Pd(II) loaded PEIS, and (b) PEIS@Pd(0). Magnified area (c) was marked as a rectangle in B. Embedded was the corresponding particle size distribution histograms based on statistical analyzes of 100 particles from TEM image. (d) TEM image of the recovered catalyst after six runs

of the amount of diphenyl product. As can be seen from the Table 3, PEIS@Pd(0) was comparable with many of others in terms of the TON and TOF. Some catalysts showed much higher TON and TOF values due to very low Pd dosages (Table 3, Entries 1 and 2).

2.4 | Transfer hydrogenation of carbonyl compounds and chalcones

Chemoselective hydrogenation is an important class of reactions that is extensively employed in the academic and

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TABLE 1 Condition optimization in model reactions^a

Entry	Pd (mol%)	Bases	Solvents	Time (h)	Yield (%) ^b
1	2	K ₂ CO ₃	EtOH	2	64
2	2	K ₂ CO ₃	H ₂ O	4	38
3	2	K ₂ CO ₃	EtOH/H ₂ O (1:1, v/v)	2	87
4	2	K ₂ CO ₃	EtOH/H ₂ O (2:1, v/v)	2	83
5	2	K ₂ CO ₃	EtOH/H ₂ O (1:2, v/v)	2	76
6	2	K ₃ PO ₄	EtOH/H ₂ O (1:1, v/v)	2	85
7	2	K ₂ CO ₃	EtOH/H ₂ O (1:1, v/v)	2	87
8	2	Na ₂ CO ₃	EtOH/H ₂ O (1:1, v/v)	2	81
9	2	NaHCO ₃	EtOH/H ₂ O (1:1, v/v)	2	48
10	2	Et ₃ N	EtOH/H ₂ O (1:1, v/v)	2	34
11	1	K ₂ CO ₃	EtOH/H ₂ O (1:1, v/v)	2	79
12	3	K ₂ CO ₃	EtOH/H ₂ O (1:1, v/v)	2	89

^aConditions: bromobenzene (2 mmol), phenylboronic acid (3 mmol), base (3 mmol), 6ml of solvent, 75°C.

^bIsolated yields



SCHEME 2 PEIS@Pd(0)-catalyzed Suzuki-Miyaura coupling reactions

 TABLE 2
 Suzuki–Miyaura coupling reaction catalyzed by

 PEIS@Pd(0)^a

Entry	\mathbb{R}^1	\mathbf{R}^2	Time (h)	Yield (%) ^b
1	Н	Н	2 (Run 1)	87
2			2 (Run 2)	89
3			2 (Run 3)	88
4			2 (Run 4)	86
5			2 (Run 5)	86
6			2 (Run 6)	85
7	Н	4-Cl	3	89
8	4-Me	Н	3	90
9	4-Br	Н	3	92
10	Н	3-NO ₂	3	87
12	4-Me	2-OMe	4	88

^aConditions: bromoarenes (2 mmol), arylboronic acid (3 mmol), PEIS@Pd(0) (2mol% Pd), K_2CO_3 (3 mmol), EtOH (3 ml) and water (3 ml), 75°C. ^bIsolated yields.

industrial researches. In catalytic transfer hydrogenations, palladium–based catalysts are considered to be the most effective.^[36] Encouraged by the impressive results for the

Suzuki reaction, we wanted to test the catalytic activity of PEIS@Pd(0) in transfer hydrogenation of carbonyl compounds with ammonium formate as an eco–friendly hydrogen donor (Scheme 3, Route A).

The scope of the reaction was firstly studied using typical carbonyl compounds as substrates. The transfer hydrogenation of structurally diverse aromatic aldehydes and ketones proceeded efficiently to give the corresponding alcohols in good to excellent yields (Table 3). The reaction rates of ketones were relatively slower than those of aldehydes perhaps due to the steric hindrance. However, even the hindered benzophenone also gave high isolated yield of product (90%) after prolonged reaction time (Table 4, Entry 9). No significant and regular electronic effects of electron-donating and electron-withdrawing substituents could be observed. Dehalogenation is a possible side reaction occurs under reductive conditions. In the case of 4-bromobenzaldehyde (Table 4, Entry 4), no dehalogenation byproduct was detected. It is worth to mention that 4-nitrobenzaldehyde gave a more complicated result. No predictable products could be detected after the consumption of starting aldehyde, instead of several unidentified byproducts.

The recyclability of the PEIS@Pd was examined in the reduction of 4-bromobenzaldehyde. The catalyst was separated from the reaction mixture by simply centrifugation after each cycle and the clear supernatant liquid was decanted slowly. The residual catalyst was washed thoroughly with ethyl acetate, followed by drying at 60°C for 2 h. Then, the catalyst was reused with a fresh charge of reactants for subsequent recycle runs under the same conditions. Desired products were obtained in 87, 90, 89, 88 and 86% yield, indicating

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Entry	Catalyst	Time (min)	Yield (%)	TON	TOF (h^{-1})	Ref.
1	Pd-Ni(20)/RGO	15	59	9687	38750	[27]
2	Pd/3-ampy-rGO	20	95	23750	71250	[28]
3	Pd–CoFe ₂ O ₄ NPs	720	79	49	4	[29]
4	Pd on aminopropyl polymethylsiloxane	360	100	50	8	[30]
5	Pd on magnetic mesoporous support	360	77	77	13	[31]
6	Pd on magnetic hollow carbon	240	97	97	24	[32]
7	Pd-CS@SiO ₂	60	90	90	90	[33]
8	Pd on biguanide SBA–15	55	99	99	119	[34]
9	Pd on hollow mesoporous spheres	480	98	98	12	[35]
10	PEIS@Pd(0)	120	87	44	22	This work

TABLE 3 A comparison of the efficiency of PEIS@Pd(0) with several supported nano Pd catalyst in Suzuki-Miyaura coupling reaction



SCHEME 3 PEIS@Pd(0)–catalyzed chemoselective transfer hydrogenation of carbonyl compounds

TABLE 4 The transfer hydrogenation of carbonyl compounds withHCOONH4 catalyzed by PEIS@Pd $(0)^a$

Entry	\mathbb{R}^1	\mathbb{R}^2	Time (h)	Yield (%) ^b
1	Н	Н	4	86
2	4-Me	Н	4	90
3	4-Cl	Н	6	91
4	4-Br	Н	6 (Run 1)	89
5			6 (Run 2)	87
6			6 (Run 3)	90
7			6 (Run 4)	89
8			6 (Run 5)	88
9			6 (Run 6)	86
10	4-OMe	Н	7	88
11	Н	Me	8	87
12	4-Me	Me	10	86
13	4-OMe	Me	10	89
14	Н	Ph	18	90

^aReaction conditions: substrates (5 mmol), HCOONH₄ (20 mmol), PEIS@Pd(0) (10% mol), CH₃CN (4 ml), H₂O (4 mL), 60°C.

^bIsolated yields.

the reused catalyst was efficient for all the six runs (Table 4, Entries 4–9).

As bifunctional ketenes with both carbonyl group and double bond, chalcones were selected to probe the chemoselectivity of PEIS@Pd in transfer hydrogenation (Scheme 3, Route B). It was found that the double bonds of chalcones were hydrogenized in 100% conversion, whereas the carbonyl groups remained untouched (Table 5). It is in accord with the previously reported results about transfer hydrogenation (HCOONH₄ or HCOOH as hydrogen donor) in the presence of homogeneous Pd–heterocyclic carbene catalyst,^[37] polymer–stabilized Pd Nps^[38] or HAP–supported Pd(0) catalyst. ^[39]

The effect of stoichiometry on chemoselectivity was thus explored as follow. After the double bonds were completely hydrogenized, more ammonium formate (equimolar to that in the first stage) was charged in the reaction mixture. After stirring for another 12 hours, the carbonyl groups still remained untouched. This fact further confirmed the chemoselectivity of this catalyst.

TABLE 5 Chemoselective transfer hydrogenation of chalcones with $HCOONH_4$ catalyzed by PEIS@Pd(0)^a

Entry	R ³	\mathbb{R}^4	Time (h)	Yield (%) ^b
1	Н	Н	12	88
2	Н	4-Cl	10	86
3	Н	2,4-Cl ₂	10	89
4	Н	2-OH	15	83
5	Н	4-OMe	15	89
6	4-OMe	Н	15	90

 aReaction conditions: chalcones (5 mmol), HCOONH4 (20 mmol), PEIS@Pd(0) (10% mol), CH3CN (4 ml), H2O (4 ml), 60°C.

^bIsolated yields.

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In conclusion, we report our investigation results on the use of polyethylenimine–grafted polysaccharide as functional support of noble metal nanocatalysts. Isocyanate–functionalized starch was attached with PEI and was loaded with Pd nanoparticles by treating the functional surface with PdCl₂, followed by reduction. TEM images revealed that the support was fully loaded with well-dispersed Pd nanoparticles. The catalyst PEIS@Pd(0) was then evaluated for the Suzuki coupling and transfer hydrogenation reactions to afford good to excellent yields. It is important to note that the supported catalyst could be recovered by simple filtration and reused at least five times without significant loss of its catalytic activity, which confirmed the good stability of the catalyst.

4 | EXPERIMENTAL

4.1 | General

All chemicals and solvents were purchased from commercial sources and used as received. Maize starch used in this work was purchased from RONGS Co. Ltd. (food grade; catalogue number: 69023738; 20–25% amylose, $ash \le 0.15\%$, lipids 0%). The PEI was purchased from Aldrich with an average molecular weight of 600. Melting points were recorded on a Buchi B-540 apparatus. FT-IR spectra were taken on a Thermo Nicolet 6700 FTIR spectrophotometer using KBr pellets. XRD patterns were recorded on a Rigaku D/MAX 2550 VB/PC diffractometer with monochromatized Cu K_{α} radiation at a setting of 40 kV and 100 mA. ¹H and ¹³C NMR spectra were measured on a Bruker AC 400 instrument in CDCl₃ using TMS as an internal standard (see Supporting Information). Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer (ionization potential 70 eV). The morphology of the samples was observed using JEOL JSM-6360 LV scanning electron microscope and JEOL JEM-1400 transmission electron microscope. The loading of palladium was determined on an Agilent 725 ES inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

4.2 | **Preparation of isocyanate-functionalized** starch

In a 250 ml round-bottomed flask equipped with a drying tube, 16.01 g (100 mmol) of p-phenylene diisocyanate was dissolved in a mixture of anhydrous acetonitrile (20 ml) and DMF (50 ml). Then 16.20 g (100 mmol glucose unit) of pre-dried maize starch was added in one portion. The resulting suspension was stirred at room temperature for 12 h. The solid was filtered, washed successively with anhydrous DMF (20 ml×3) and anhydrous ethyl acetate

 $(20 \text{ ml}\times3)$ to remove unreacted isocyanate, and dried under vacuum at 40°C for 2h. Desired isocyanate–functionalized starch was obtained as a white powder (26.80 g).

4.3 | Preparation of polyethyleneimine grafted starch (PEIS)

14.00 g of isocyanate–functionalized starch was suspended in a solution of 14.00 g polyethyleneimine in 50 mL anhydrous acetonitrile. The mixture was stirred at room temperature for 3 h. The grafted starch was collected by filtration and washed with acetonitrile (10 ml×4). After being dried under vacuum, 19.92 g of PEIS was obtained as free–flowing white powders.

4.4 | Preparation of PEIS@Pd(0)

To a suspension of PEIS (1.00 g) in 5 ml of acetonitrile was added 0.18 g (1 mmol) of palladium chloride. The mixture was stirred at 40°C for 12 h. Then 20 ml of ethanol containing 76 mg (2 mmol) of sodium boronhydride was slowly dropped into the suspension under vigorous stirring. After 2 h of reduction, the products were obtained by filtration, washed thoroughly with deionized water (10 mL×3) and ethanol (10 ml×3). Following the product was dried under vacuum to obtain PEIS@Pd(0) as a black powder (1.10 g).

4.5 | General procedure for the Suzuki– Miyaura coupling catalyzed by PEIS@Pd(0)

Arylboronic acid (3 mmol), substituted bromobenzene (2 mmol), K_2CO_3 (0.41 g, 3 mmol) and 44 mg (2% mol) of PEIS@Pd(0) were added to a 20 mL reaction vial containing EtOH (3 mL) and water (3 ml). The mixture was stirred at 75°C for a specified period as monitored by TLC or GC (Table 2). On completion of the reaction, the mixture was filtered and the catalyst was washed successively with water (1 mL) and EtOH (1 ml). The combined filtrate was then extracted by ethyl acetate (3 ml×3). Combined organic layer was then dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of EtOAc: PE (v/v = 1: 10) to give pure product.

4.6 | General procedure for the transfer hydrogenation catalyzed by PEIS@Pd(0)

To a solution of HCOONH₄ (1.26 g, 20 mmol) in CH₃CN (4 ml) and water (4 ml) was added 0.55 g (10% mol) of Pd(II) loaded PEIS. The mixture was stirred at 60°C for 30 min (the color of catalyst changed from yellow–gray to black rapidly). Afterwards 5 mmol of carbonyl compounds (aldehydes, ketones or chalcones) was then introduced into the reaction vessel. The stirring continued to the appropriate time as

monitored by TLC or GC (Table 2 and 3). On completion of the reaction, the mixture was filtered and the catalyst was washed with ethyl acetate (3 ml×3). The aqueous filtrate was then extracted by ethyl acetate (3 ml×3). Combined EA extracts was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of EtOAc: PE ($\nu/\nu = 1$: 10) to give pure product.

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