FULL PAPER



Polymer-supported palladium: A hybrid system for multifunctional catalytic application

Abu Taher | Meenakshi Choudhary | Debkumar Nandi 🗅 | Samarjeet Siwal | Kaushik Mallick 🗅

Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa

Correspondence

Kaushik Mallick, Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa. Email: kaushikm@uj.ac.za

Funding information National Research Foundation (NRF), South Africa Polymer-supported palladium was synthesized by applying a single-step wet chemical synthesis route and the resultant composite material was characterized by means of various techniques. Infrared and UV–visible spectra provided information on the chemical structure of the polymer. Microscopy techniques showed the general morphology of the polymer. The oxidation state of palladium was determined using the X-ray photoelectron spectroscopy method. The synthesized material was applied as a heterogeneous catalyst for the Heck coupling reaction and also as an electrocatalyst for the oxidation of cysteine.

KEYWORDS

cysteine oxidation, Heck coupling reaction, polymer-supported palladium, single-step synthesis

1 | INTRODUCTION

The evolution of innovative materials and new fabrication techniques has become a matter of success for various areas of research activities. Metal-containing polymers^[1] hold a lot of promise as they exhibit novel properties, such as magnetic^[2] and semiconductor^[3] properties, and have potential applications in sensors^[4] and organocatalysis reactions.^[5] Among the various organocatalysis reactions, carbon-carbon (C--C) coupling reactions, through transition metal catalysis routes, have been developed because of their real-world applications for the synthesis of organic building blocks, fine chemicals, pharmaceuticals and biologically active compounds.^[6] Palladium catalyses various coupling processes, such as Suzuki, Heck and other common reactions, generally performed in the presence of homogeneous palladium species, which results undesirable palladium contamination in products.^[7] For that reason, a support is an important factor in designing a heterogeneous catalyst system for practical implementation. Efforts have been made towards the development of palladium complex catalysts and palladium nanoparticle catalysts supported on metal oxides, carbon-based materials, zeolites, mesoporous materials, layered materials and polymer composites for various C--C coupling reactions.^[8] In general, support materials provide a way for

the easy recycling of the catalyst, but in many cases the surface area and pH value directly influence the catalytic performance. In addition, the robust nature of the supports and their abilities in stabilizing the active centres are the crucial requirements for long-lasting catalytic performance.

Various types of inorganic material and organic molecules or polymers have been applied as matrices to stabilize both ionic and metallic palladium. Due to the unique properties of polymers, they are often used as hosts for the appropriate palladium species. A modified starch, a biopolymer, served as a support of Pd(0) and performed as an active catalyst for Suzuki, Heck and Sonogashira coupling reactions.^[9] Polystyrene-supported palladium nanoparticles were also used as a potential catalyst for various C--C coupling reactions, whereas a recyclability study showed a considerable decrease of yield in successive reactions and was due to the leaching of palladium species during the reaction.^[10] A relatively low-leaching and moisture-stable polystyrene-supported palladium complex catalyst was reported for the Suzuki reactions at room temperature under aerobic conditions.^[11] Polystyrene containing functionalized heterocycles can also be a good candidate for the immobilization of Pd(II) species and showed good catalytic activity and reusability for the Suzuki reaction.^[12] A polyacrylamide-based Pd(II) catalyst has been reported for the Heck reaction with high catalytic recycling efficiency.^[13] Monodispersed palladium nanoparticles in poly(N-vinyl-2pyrrolidone) showed activity towards the coupling reaction between iodo-/bromobenzene and butyl acrylate.^[14] Polypyrrole is a conducting organic polymer that in combination with appropriate noble metal nanoparticles produces composites, which exhibit catalytic activity.^[4] A 'core-shell' type of structure with 'polystyrene in the core' and 'palladium-polypyrrole nanocomposite as the shell' has been employed for Suzuki and Heck cross-coupling reactions in water.^[15] Polyaniline as well as its derivatives are conducting organic polymers and have also been demonstrated as supports for immobilizing palladium species for various carbon-carbon bond formation reactions.^[16, 5] In our previous study we found that polymer-encapsulated palladium nanoparticles served as an efficient catalyst for the Suzuki coupling reaction in the absence of phosphine ligand.^[17]

In this report, we describe the formation of a supramolecular composite of mono-valent palladium and polymeric form of 4-thiophen-3-ylaniline, Pd-pAT, using the *in situ* polymerization and composite formation approach.^[18] The composite system was characterized using optical, microscopic and non-destructive surface characterization techniques. The supramolecular material was used as a catalyst for the Heck coupling reaction under phosphine-free reaction conditions and also used as an electrocatalyst for the oxidation of cysteine.

2 | EXPERIMENTAL

2.1 | Materials

Analytical-grade chemicals and solvents were used in the experiments without further purification.

2.2 | Material characterization

Microscopy studies of the synthesized material were performed using a JEOL JEM-2100 analytical electron microscope. Surface images were obtained using a JEOL JSM-840 scanning electron microscopy (SEM) instrument operating at an accelerating voltage of 20 kV. Surface properties of the material were characterized using a Shimadzu XD-3A X-ray diffractometer and X-ray photoelectron spectra (XPS) were collected using a Physical Electronics 560 ESCA/SAM instrument. Optical properties of the synthesized material were measured using Shimadzu IRAffinity-1 and Shimadzu UV-1800 spectrophotometers. Electrochemical studies was carried out with a potentiostat (Bio-Logic SP-200) connected to a data controller, with a glassy carbon electrode (GCE) as the working electrode. A Bruker UltraShield-400 was used to record ¹H NMR and ¹³C NMR spectra.

2.3 | Preparation of Pd-*p*AT composite catalyst

In a typical experiment, 3.5 ml of K_2PdCl_4 (from a stock solution of 0.0326 g of K_2PdCl_4 in 10 ml of water) was added dropwise to 4-thiophen-3-ylaniline (0.350 g in 10 ml of CH₃OH). A yellow precipitate was formed at the bottom of the reaction pot. The solid material was characterized using various optical, surface and microscopic techniques and also applied as a catalyst for Heck coupling reactions and electrochemical cysteine oxidation reaction.

2.4 | General procedure for Pd-*p*AT-catalysed Heck coupling reaction

In a typical experiment, aryl halide (1.0 mmol), alkene (1.5 mmol), KOAc (147 mg, 1.5 mmol) and the palladium–polymer (Pd-*p*AT) catalyst (5.0 mg, 0.050 mol% Pd) were added to dimethylformamide (DMF; 2 ml) in a round-bottom flask at 100 °C for 8 h. The reaction was followed using the TLC technique.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of compound

The optical properties of the synthesized material were characterized using UV-visible and Fourier transform infrared (FTIR) spectroscopic methods. The UV-visible spectrum (Figure 1a) for Pd-*p*AT shows absorption peaks at around 320 nm which is attributed to the π - π * transition associated with benzenoid rings. A broad band within the range 400–500 nm is accounted for by the polaron–bipolaron transition. The presence of a quinoid unit in the polymer composite is confirmed from the FTIR spectrum (Figure 1b)



FIGURE 1 (a) UV-visible and (b) FTIR spectra of Pd-pAT composite

and which is associated with the vibrational peak at 1658 cm $^{-1}$. A doublet band in the range between 1410 and 1450 cm⁻¹ can be attributed to the ν_3 vibration of thiophene segment.^[19] Figure 2(a), an SEM image, shows the general morphology of the synthesized supramolecular composite, whereas Figure 2(b) shows a transmission electron microscopy (TEM) image for the same material. In the TEM image, a smooth surface is noticed without evidence of the formation of palladium nanoparticles. Energy-dispersive X-ray spectroscopy (EDS) was conducted by focusing the electron beam on different areas of the investigated material and the characteristic palladium X-ray peaks are observed around 3.0 keV (Figure 3a). XPS was employed to investigate the chemical state of palladium. A high-resolution XPS Pd 3d spectrum, for the Pd-pAT sample, with the core level split into $3d_{5/2}$ and 3d_{3/2} components due to a spin-orbit interaction is shown in Figure 3(b). Here, the binding energy value associated with the Pd 3d_{5/2} line was estimated to determine the valence state of palladium. In general, the peaks at 335.7 and 337.75 eV correspond to metallic and bi-valent state of palladium, respectively.^[20] In Figure 3(b), after



FIGURE 2 (a) SEM and (b) TEM images of Pd-pAT composite



FIGURE 3 (a) EDS spectrum of Pd-*p*AT composite. The presence of palladium is evident from the signal AT *ca* 3.0 keV. (b) XPS signal of Pd-*p*AT composite. The peak at 337.56 eV is due to the presence of unreacted Pd(II) whereas the peak AT 336.74 eV indicates the presence of Pd(I) within the sample

deconvolution of the spectrum within the range 335.0-340.0 eV, two separate peaks at 337.56 and 336.74 eV become visible and those correspond to bi-valent and mono-valent state of palladium, respectively. The intensity and area of the band with the peak positioned at 336.74 eV are higher than those of the band at 337.56 eV, indicating the presence of higher concentration of Pd(I) in the Pd-*p*AT sample.

The detailed mechanism of composite formation has been reported elsewhere.^[18] The chemistry of mono-valent palladium-containing complexes is potentially important in various catalytic process applications.^[21]

3.2 | Catalytic property of Pd-*p*AT

The catalytic property of the synthesized material was investigated in terms of a carbon–carbon bond formation reaction. Among the various C–C bond formation reactions, Heck coupling is one of the important for its diverse applications in the fine chemical and pharmaceutical industries. The same composite material, Pd-pAT, was also used as an electrocatalyst for the voltammetric detection of L-cysteine (CySH), an important amino acid performing a critical role in biological systems.

3.3 | Performance of Pd-*p*AT in the Heck reaction

The presence of a base in the reaction media is very important for the Heck reaction and a series of bases, namely K₂CO₃, Na₂CO₃, KOAc, KO^tBu, Cs₂CO₃ and K₃PO₄, were used to find the optimum conditions for the reaction. We find that KOAc acts as a highly efficient base for the current coupling reaction when Pd-pAT is applied as a catalyst. Again, the selection of a suitable solvent is also an important issue for organic reactions. Among the various solvents, namely Dimethylformamide (DMF), Dimethylacetamide (DMA), N-methyl-2-pyrrolidone, toluene, dimethylsulfoxide and EtOH-H2O (1.0:1.0), used for this experiment, we find that DMF performs efficiently when combined with KOAc and the combination of DMF and KOAc produces the highest yield of desired product 3cb for the current Heck reaction between 4-iodoanisole (1c) and methyl acrylate (2b) in the presence of 0.050 mol% Pd from the Pd-pAT catalyst (supporting information, Table 1S, entry 4). We also find that by decreasing or increasing the amount of catalyst no further improvement of the product, in terms of yield, is obtained. Based on the above optimized reaction conditions, we explored the versatility of the catalyst with diverse examples of aryl halides and activated alkenes (Table 1). All the substrates produce the expected products with very good to excellent yields and selectivity.

An almost identical yield is obtained when styrene is coupled with iodobenzene and 4-methyliodobenzene to produce the desired products **3aa** and **3ba** with 90 and 92% yields, respectively (Table 1). It is important to mention that the presence of electron-donating and electron-withdrawing group does not have any effect on yield for the reactions since 4-methoxyiodobenzene (**1c**) or 4-nitroiodobenzene (**1d**) couple with styrene (**2a**) to produce 1-methoxy-4-styrylbenzene (3ca) and 1-nitro-4-styrylbenzene (3da) with yields of 98 and 97%, respectively. A similar trend is noticed for the coupling reactions when styrene is replaced with 2b (Table 1, products 3ab-3db). In our current study, when acrylonitrile is used as one of the coupling partners with various substituted aryl halides a moderate to good yield is observed from 77 to 85% for the desired coupling products 3 cc, 3 dc and 3ec (Table 1). The reaction between 2methyliodobenzene (1e) and acrylonitrile (2c) produces the coupled product 3-o-tolylacrylonitrile (3ec) with a yield of 83%. Similarly, 1c and 1d when coupled with 2c produce the compounds 3-(4-methoxyphenyl) acrylonitrile (3 cc) and 3-(4-nitrophenyl) acrylonitrile (3 dc) with yields of 80 and 85%, respectively. In the current Heck coupling reaction, for the aryl halide component, when iodo group is replaced with bromo group the yield of coupled product decreases because of the presence of stronger C-Br bond compared with C-I bond (Table 1).

3.4 | Mechanism, recyclability and metal leaching studies for Heck reaction

The Heck reaction is a cross-coupling reaction of an aryl halide with an alkene to make a substituted alkene using palladium as a catalyst in the presence of a base.^[22] The reaction begins by oxidative addition of the aryl halide to the palladium, followed by the coordination of alkene segment to the palladium and that finally produces the aryl–alkene coupled product through the reductive elimination of Pd(0).

The recyclability as well as the scaling up of the Heck reaction using the Pd-*p*AT composite material as a catalyst was investigated for the coupling of **1d** with **2a** (**1d**: 10.0 mmol; **2a**: 15.0 mmol; catalyst (Pd-*p*AT): 50 mg (0.05 mol% Pd); temperature: 100 °C; time: 8 h). After the first cycle, a product yield of 95% was achieved and the recovered catalyst was used for another four times under the same reaction conditions. At the end of the fifth cycle, a yield

TABLE 1 Heck coupling reaction of olefins with aryl halides^a



^aReaction conditions: aryl halide (1.0 mmol), alkene (1.5 mmol), KOAc (147 mg, 1.5 mmol), DMF (2 ml). For aryl halides ($X = Br^{-}$): catalyst concentration of 0.075 mol% Pd. All reactions were carried out at 100 °C for 8 h. Isolated yields are presented.

of 81% of 1-nitro-4-styrylbenzene was achieved (Figure 4a). The X-ray diffraction pattern of the recovered catalyst is shown in Figure 4(b). The observed peaks located at 40.10°, 45.60°, 67.50° and 81.0° representing the (111), (200), (220) and (311) Bragg reflection planes of a face-centred cubic lattice, respectively, confirm the presence of metallic palladium nanoparticles in the recovered catalyst.^[23] The TEM image (Figure 4c) shows the formation of palladium nanoparticles with an average size of 20 nm. The gradual decrease of yield with the number of cycles is possibly due to the leaching of the palladium species from the support and also due to the loss of composite catalyst during the filtration process in each cycle. The total amount of metal leached was assessed using the inductively coupled plasma mass spectrometry technique where the estimated



FIGURE 4 (a) histogram generated from recyclability study for Heck reaction. (b) typical X-ray diffraction pattern of the used catalyst (recovered after the fifth cycle of reaction). (c) TEM image of the used catalyst at the end of the fifth cycle for the Heck coupling reaction reveals the formation of palladium nanoparticles with an average size of 20 nm

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concentration of the leached palladium is found to be 3.5 and 23.0 ppm, during the first and fifth cycle, respectively. In this work, we find that the Heck coupling reaction is feasible between olefins and both aryl iodide and bromide in the presence of 0.050 and 0.075 mol% Pd, respectively, at 100 °C for 8 h. For aryl chloride, we observe that a higher concentration of catalyst (0.5 mol% Pd) is required for the coupling reaction at 120 °C for a period of 12 h with a yield of 25%. We also find that at 120 °C the polymer-based catalyst loses its performance after the first cycle of the reaction.

3.5 | Electrocatalytic performance of Pd-*p*AT for detection of CySH

CySH is a thiol group-containing amino acid, and has been extensively used in the medicine and food industries. On oxidation, it forms cystine (CyS-SCy) with a disulfide bond. The cysteine-cystine couple can act as a redox switch in a variety of biological systems^[24] and therefore the quantitative detection of CySH and an understanding of the oxidation mechanism are important in protein chemistry^[25] and also has drawn considerable attention.^[26] The electrochemical technique is a sensitive and convenient method for the quantitative detection of many biologically active molecules. CySH oxidation and detection on the surface of an unmodified electrode suffer because of electrode corrosion, lack of sensitivity and high value of oxidation potential. These problems can be potentially overcome using a suitable electrocatalyst as an electrode modifier.

Transition metals have an important role as catalysts for various reactions including electrochemical reactions.^[27] In this current study, we applied Pd-*p*AT as an electrocatalyst for the electrochemical recognition of CySH.

Cyclic voltammetry was used to study the electrochemical properties of a Pd-pAT-modified working electrode. Shown in Figure 5(a) are voltammograms for bare GCE in the absence (curve 'a') and in the presence (curve 'b') of 40 µM CySH. The intensity of the current for curve 'b' is increased, which indicates the oxidation of CySH on the bare electrode. To check the performance of the composite system, we used Pd-pAT-modified working electrode as a sensing device for CySH detection. Figure 5(b) shows the voltammograms of Pd-pAT-modified working electrode in the absence (curve 'a') and in the presence (curve 'b') of 40 µM CySH (analyte). The voltammogram in the presence of analyte shows higher current value at lower potential range. The differential pulse voltammetry technique was applied, using different concentrations of analyte, for further confirmation of the cyclic voltammetry results. With increasing concentration of CySH (40, 80, 120, 160 and 200 µM), the current signal (curves 'b'-'f', respectively) increases gradually as evidenced by differential pulse voltammograms



FIGURE 5 Cyclic voltammograms for (a) bare working electrode and (b) Pd-*p*AT-modified working electrode in the absence (curve 'a') and presence (curve 'b') of 40 μ M cysteine. (electrolyte: 10 mM phosphate buffer; scan rate: 50 mV s⁻¹)



FIGURE 6 (a) Voltammograms of differential pulse voltammetry study for Pd-*p*AT-modified GCE with increasing concentrations of cysteine: Curves 'b'-'f' for 40, 80, 120, 160 and 200 μ M cysteine, respectively. Curve 'a' is the voltammogram in the absence of cysteine. Differential pulse voltammetry was conducted with a pulse width of 50 ms and scan rate of 0.05 V s⁻¹. (b) regression coefficient plot

(Figure 6a) and the current signal shows a linear correlation, with a regression coefficient value of 0.9965, for CySH from 40 to 200 μ M (Figure 6b). The sensitivity of Pd-*p*AT-modified GCE for the detection of CySH is found to be 174 μ A mM⁻¹ cm⁻². A chronoamperometry study was also performed using Pd-*p*AT-modified working electrode in the absence of CySH (Figure 7, curve 'a'). The



FIGURE 7 Voltammograms of chronoamperometry study for PdpAT-modified GCE with a fixed potential 0.5 V for a period of 20 s. Curve 'a' represents the voltammogram in the absence of cysteine and curves 'b'-'e' represent the voltammograms in the presence of cysteine with the concentrations of 40, 80, 120 and 150 μ M, respectively. Curves 'f'-'i' represent the voltammograms in the presence of tryptophan, glycine, histidine and leucine, respectively, with concentrations of 40 and 150 μ M, and indicate the irresponsive nature towards the current signal

chronoamperometry voltammograms (Figure 7), as represented by curves 'b'-'e', are for different concentrations of CySH, namely 40, 80, 120 and 150 μ M, respectively, and which indicate that current intensity is directly proportional to the CySH concentration for the Pd-*p*AT electrocatalyst. We also investigated the universality of the Pd-*p*AT catalyst by the addition of some potential interfering species, like tryptophan, glycine, histidine and leucine. A passive nature is found for the catalyst towards all the biomolecules, with various concentrations (curves 'f'-'i'), used as the interfering species in this experiment.

The mechanism of CySH detection can be represented by the following equations, where the first step corresponds to the oxidation of univalent palladium and the second step involves CySH oxidation with the formation of cystine (CyS–SCy) followed by the subsequent reduction of palladium ion to zero-valent palladium:

$$Pd(I) \rightarrow Pd(II) + e^{-1}$$
 (1)

$$Pd(II) + 2CySH \xrightarrow{-[2H]} CyS - SCy + Pd(0)$$
(2)

The occurrence of the above mechanism can be evidenced from an electron microscope image (Figure 8) of the material recovered from the working electrode, where tiny particles, within the range 2–5 nm in size, are visible on the polymer matrix (some representative particles are shown within circles).



FIGURE 8 Polymer-stabilized palladium nanoparticles within the range 2–5 nm in size (sample collected from the working electrode at the end of the experiment)

4 | CONCLUSIONS

The present article reports the synthesis of a functional polymer-based palladium composite for application in the Heck coupling reaction under phosphine-free conditions. The synthesized material was also used as an electrocatalyst for the detection of cysteine using the differential pulse voltammetry technique and the sensitivity of the palladium–polymer catalyst for the detection of cysteine was found to be 174 μ A mM⁻¹ cm⁻². A chronoamperometry study simultaneously showed the active behaviour towards the detection of cysteine with various concentrations and passive behaviour with some biomolecules like tryptophan, glycine, histidine and leucine. The mechanism for both Heck coupling and cysteine oxidation indicates the formation of palladium nanoparticles, which corroborates the experiment results and is evidenced by the microscopic techniques.

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SUPPORTING INFORMATION

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