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ORIGINAL ARTICLE

Synthesis of palladium nanoparticles with leaf extract of *Chrysophyllum cainito* (Star apple) and their applications as efficient catalyst for C–C coupling and reduction reactions

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Abstract A simple green chemical method for the one-step synthesis of palladium nanoparticles (PdNPs) has been described by reducing palladium (II) chloride with the leaf extract of *Chrysophyllum cainito* in aqueous medium. The synthesis of the palladium nanoparticles completed within 2–3 h at room temperature, whereas on heat treatment (70–80 °C), the synthesis of colloidal PdNPs completed almost instantly. The stabilized PdNPs have been characterized in detail by spectroscopic, electron microscopic and light scattering measurements. The synthesized PdNPs have been utilized as a green catalyst for C–C coupling reactions under aerobic and phosphine-free conditions in aqueous medium. In addition, the synthesized PdNPs have also been utilized as a catalyst for a very efficient sodium borohydride reduction of 3- and 4-nitrophenols. The synthesized PdNPs can retain their catalytic activity for several months.

Keywords Palladium nanoparticles · *Chrysophyllum cainito* · Polyphenols · Green catalyst · C–C coupling

Introduction

Nanotechnology, which includes multi-dimensional aspects of nanoparticles, has created a tremendous impact in diversified fields such as pharmacology, biodiagnostics, medicine, drug-delivery, catalysis, etc. in the recent past [1–9]. Among various transition metal nanoparticles (MNPs), the palladium nanoparticles (PdNPs) have drawn significant attention of the scientific community because of its efficiency as a catalyst for C–C coupling reactions which is one of the most powerful transformations in organic chemistry [10–17]. In the synthesis of PdNPs, the use of the proper stabilizing agents is crucial to maintain the active surface of the nanoparticles as well as to avoid the formation of less-active palladium black [10]. Moreover, for the sustainable development, the synthesis of the metal nanoparticles via eco-friendly green method which includes the use of nontoxic and biocompatible precursors under very mild conditions is the need of the time [18–25]. However, the green synthesis and stabilization of surface active PdNPs by non-toxic renewable chemicals and its utilization for C–C coupling and reduction reactions in environment friendly conditions is not very common in literature [26–32]. In this manuscript we have utilized the leaf extract of medicinal plant *Chrysophyllum cainito,* rich in polyphenols [33, 34], as reducing as well as stabilizing agent for the synthesis and stabilization of surface active colloidal PdNPs. The synthesized PdNPs were characterized by surface plasmon resonance (SPR) spectroscopy, high-resolution transmission electron microscopy (HRTEM), dynamic light scattering (DLS) and X-ray diffraction studies. The synthesized colloidal PdNPs were successfully utilized as catalyst for the Suzuki and Heck coupling reactions under aerobic, phosphine-free conditions in aqueous medium. In addition, the synthesized

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colloidal PdNPs have been successfully utilized for the sodium borohydride ($NaBH_4$) reduction of 3-nitrophenol (3-NP) and 4-nitrophenol (4-NP) to the corresponding aminophenols in aqueous medium. The kinetics of these reduction reactions were studied spectrophotometrically.

Experimental

Materials

The leaves of *C. cainito* were collected from a garden of northern east part of Thailand. $PdCl_2$ was purchased from Alfa Aesar Company and phenyl boronic acid was purchased from Sisco Research Laboratory Pvt. Ltd. (SRL), India. Methyl acrylate and 3-nitrophenol were purchased from Loba Chemie Pvt. Ltd., India. Iodobenzene was purchased from Spectrochem Pvt. Ltd., India. K_2CO_3 is from E Merck (LR). 4-Nitrophenol was purchased from Merck. All these chemicals were used without further purification. All commercial-grade solvents were purified by distillation before use.

Methods

Preparation of the C. cainito leaf extract

Leaf extract of *C. cainito* was prepared by following a method already reported from our laboratory which yielded crystalline green solid (0.974 g).

The greenish crystalline solid (0.005 g) was dissolved in distilled water (10 mL) to get a semi-transparent solution (500 mg L^{-1}) [31].

Synthesis of palladium nanoparticles

Aliquots of Pd (II) solution (0.2 mL, 8.07 mM each) were charged to the leaf extract solutions of *C. cainito* to prepare a series of stabilized PdNPs where concentration of the leaf extract varied from 80 to 400 mg L^{-1} and the concentration of Pd (II) was fixed at 1.614 mM.

Suzuki coupling reaction

Iodobenzene (55 μL, 0.49 mmol), phenylboronic acid (91.5 mg, 0.75 mmol), K_2CO_3 (135 mg, 0.98 mmol), H_2O (0.769 mL) and colloidal PdNPs stabilized by *C. cainito* leaf extract (0.231 mL, 0.077 mol% of Pd with respect to iodobenzene) were taken into a 25-mL round bottom flask. The reaction mixture was heated at 90 °C in an oil bath with continuous stirring for 12 h. The progress of the reaction was monitored by TLC using petroleum ether as the eluent. Every time the formation of the product was monitored under UV light as the product biphenyl was UV active compound. After 12 h the reaction mixture was cooled at room temperature and the reaction mixture was diluted with diethyl ether and the total reaction mixture was taken into a separating funnel to separate the aqueous layer (10 mL, 2 times). Then the ether layer was washed with brine solution (5 mL). The ether layer was dried and the crude product was obtained as whitish solid material. Then the crude product was purified by column chromatography by using petroleum ether as eluent. The yield of the product biphenyl was 99.47%. NMR data: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 (d, 4H), 7.51 (t, 4H), 7.33 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.28, 128.29, 127.82, 127.21.

Heck coupling reaction

Iodobenzene (0.112 mL, 1 mmol), methyl acrylate (0.136 mL, 1.5 mmol), DMF (0.2 mL) and distilled water (0.6 mL) were taken in a 25-mL round bottom flask. Then colloidal PdNPs stabilized by *C. cainito* leaf extract (0.610 mL, 0.1 mol% of Pd with respect to iodobenzene) was added to it. The reaction mixture was placed into an oil bath and stirred at around 70 °C for 5 h. The process of the reaction was monitored by TLC using 5% ethyl acetate/petroleum ether as eluent. The formation of the product was monitored under UV light as the product was UV active. After 5 h the reaction mixture was cooled at room temperature and diluted with diethyl ether (30 mL). Then the total reaction mixture was taken into a separating funnel to separate the water layer. Then the reaction mixture was washed with 2 N HCl solution (5 mL) and brine solution (5 mL, 2 times), respectively. The ether layer was dried and the crude product was obtained as a liquid material. The crude product was purified by column chromatography using 5% ethyl acetate/petroleum ether as eluent. NMR data: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (d, 1H, $J = 16.0$ Hz), 7.28-7.56 (m, 5H), 6.45 (d, 1H, $J = 16.4$ Hz), 3.83(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.42, 144.87, 130.27, 128.87, 128.05, 117.83, 77.33, 76.99, 76.67, 51.67.

Results and discussion

Study of the physicochemical properties

To know about the size distribution and stability of the stabilized PdNPs synthesized with varied amount of the leaf extract of *C. cainito,* the dynamic light scattering experiments (DLS) were performed.

The hydrodynamic diameters of the PdNPs were in the range of 169.24 nm when the concentration of the leaf extract was 100 mg L^{-1}. When the concentration of the leaf extract was 200 mg L^{-1}, the hydrodynamic diameters were decreased to 59.18 nm due to the better stabilization of the small-sized PdNPs by the leaf extract (see supporting information Fig. S1). However, when the concentration of the leaf extract was further increased (400 mg L^{-1}), the hydrodynamic diameter of the PdNPs was further increased (94.76 nm). This is due to the presence of larger number of ligands present on the surface of PdNPs in case of higher concentration of the leaf extract because in dynamic light scattering (DLS) measurement, the instrument cannot measure the bare PdNPs which is possible in case of HRTEM study. The data obtained were highly reproducible on repeated measurements with freshly prepared batch of PdNPs.

We have also measured the surface charge (zeta potential) of the PdNPs synthesized with varied concentration of the leaf extract (100–400 mg L^{-1}) to know about the stability of the PdNPs (see supporting information Fig. S1). In all the cases, the surface charges were in the range of $-$ 19 to $-$ 20 mV. These high negative values of the zeta potential indicated the presence of high electrical charge on the surface of the PdNPs which prevent the further aggregation of the nanoparticles due to repulsive interactions. So, because of this high negative value of the Zeta potential, the PdNPs synthesized with the leaf extract of the *C. cainito* were highly stable.

To confirm the formation of colloidal PdNPs, UV–Visible spectroscopic studies of the colloid samples were performed (Fig. 1). A characteristic continuous surface plasmon resonance (SPR) band in the UV–Visible region was observed for each colloidal sample confirming the formation of the PdNPs. Initially the intensity of the SPR band increased with the increasing concentration of the leaf extract as stabilizing agent but no further increase in the intensity was observed when the concentration of the leaf extract reached 200 mg L^{-1}.

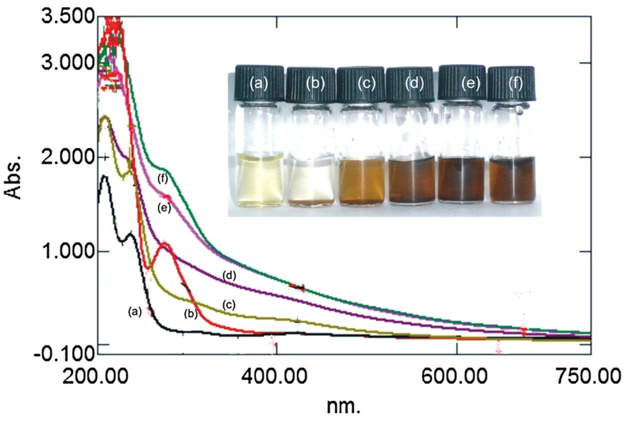

Fig. 1 UV–Visible spectra of: (a) aqueous $PdCl_2$, (b) leaf extract of *C. cainito*, (c–f) colloidal PdNPs synthesized and stabilized with 80, 100, 200, 400 mg L^{-1} concentrations of *C. cainito* leaf extract, respectively. Inset: Photograph of the vials containing Pd (II) solution, plant extract and colloidal PdNPs stabilized by 80, 100, 200, 400 mg L^{-1} concentrations of *C. cainito* leaf extract (after 18 h of mixing, from left to right)

Characterization of colloidal PdNPs

HRTEM studies

To characterize the size, shape and morphology of the colloidal PdNPs synthesized and stabilized with the leaf extract of *C. cainito*, we performed HRTEM analysis. HRTEM analysis revealed that at 200 and 400 mg L^{-1} concentrations of the reducing and stabilizing agents, flower-like aggregates of colloidal PdNPs were formed (Fig. 2a–f). The flower-like aggregates were composed by the self-assembled discrete palladium nanoparticles coming from multiple directions. Energy dispersive X-ray (EDX) analysis of the synthesized colloidal PdNPs confirmed that the nanoparticles are composed of crystalline Pd (Fig. 2g). A strong band of carbon and oxygen indicated the presence of biomolecules on the surface of PdNPs which have played a role in the reduction of Pd (II) and stabilization of PdNPs. Selected area electron diffraction (SAED) pattern of a PdNP also confirmed the formation of crystalline palladium nanoparticles (Fig. 2h).

XRD studies

The wide-angle X-ray diffraction studies of colloidal PdNPs synthesized and stabilized with *C. cainito* were carried out after coating the samples on a glass slide and removal of the volatiles under bulb. The crystallinity of colloidal PdNPs was confirmed with characteristic reflection of 111, 200, 220 and 311 plane at $2\theta = 29.70°, 46.55°, 67.69°, 81.57°$ (Fig. 3). These values are in agreement with the reported JCPDS file no. 05-0681 for face-centred cubic crystalline palladium [35, 36].

Applications

C–C coupling reactions

To check the efficacy of the colloidal PdNPs synthesized and stabilized with the leaf extract of *C. cainito* as catalyst for C–C coupling reactions, we have performed (a) the Suzuki reaction and (b) the Heck reaction:

(a) Suzuki reaction
The Suzuki coupling reaction between iodobenzene (55 μL, 0.49 mmol) and phenylboronic acid (91.5 mg, 0.75 mmol) was carried out in the presence of colloidal PdNPs stabilized by *C. cainito* leaf

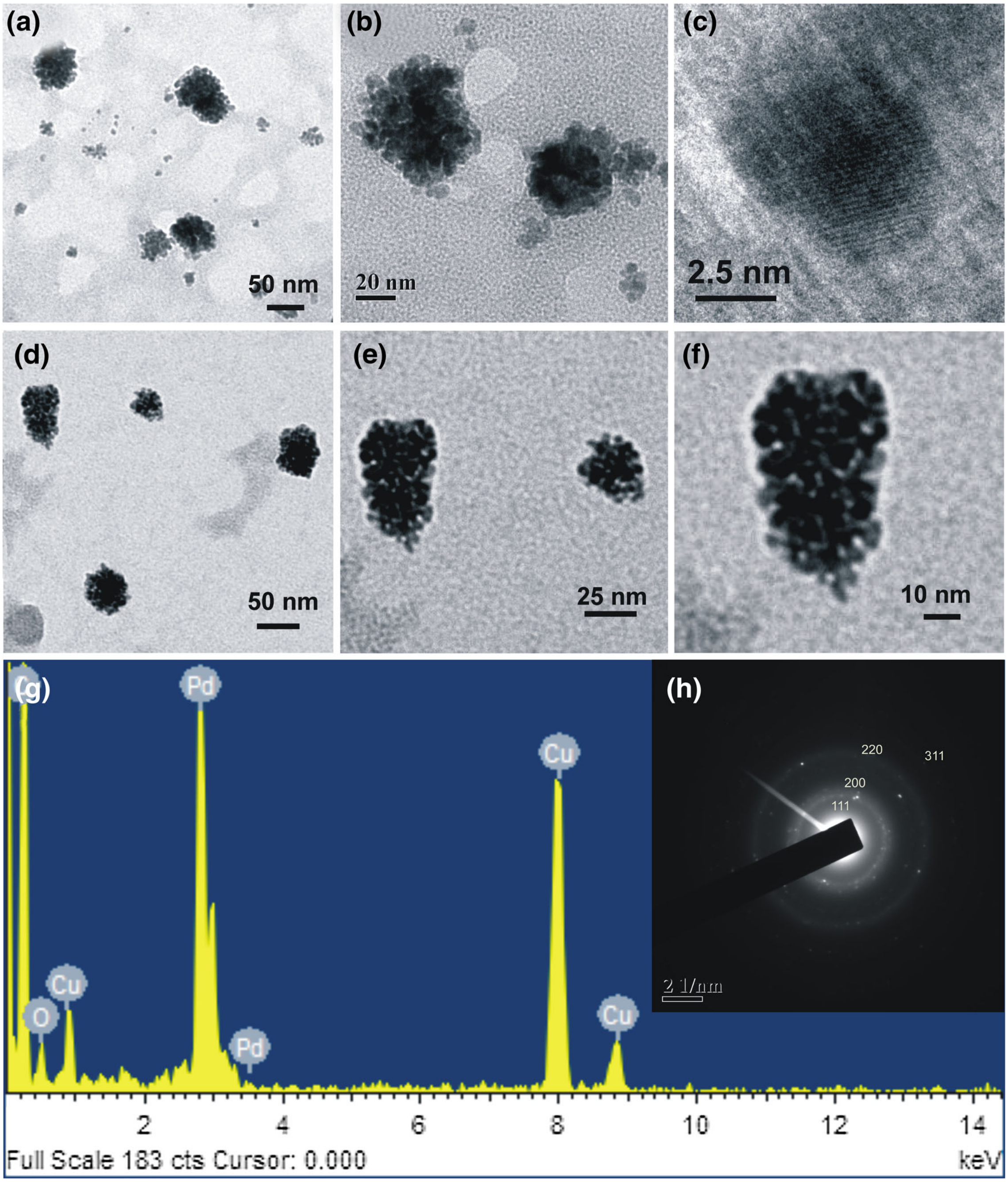

Fig. 2 HRTEM images of the colloidal PdNPs (**a**–**c**) synthesized and stabilized with leaf extract of *C. cainito* (200 mg L^{-1}); **d**–**f** synthesized and stabilized with leaf extract of *C. cainito* (400 mg L^{-1}); **g** elemental analysis of colloidal PdNPs by energy dispersive X-ray (EDX); **h** SAED of a PdNP

extract (0.231 mL, 0.077 mol% of Pd with respect to iodobenzene) as catalyst and K_2CO_3 (135 mg, 0.98 mmol) as a base in aqueous medium at 90 °C. The progress of the reaction was monitored under UV light as the product biphenyl was UV active compound. The complete conversion occurred in 12 h. The product was extracted with petroleum ether and purified by column chromatography. The yield was 99.47%. The purified product was characterized by NMR spectroscopy.

(b) Heck reaction

The Heck coupling reaction between iodobenzene (0.112 mL, 1 mmol) and methyl acrylate (0.136 mL, 1.5 mmol) was carried out in the presence of colloidal PdNPs stabilized with the leaf extract of *C. cainito* as catalyst (0.610 mL, 0.1 mol % of Pd

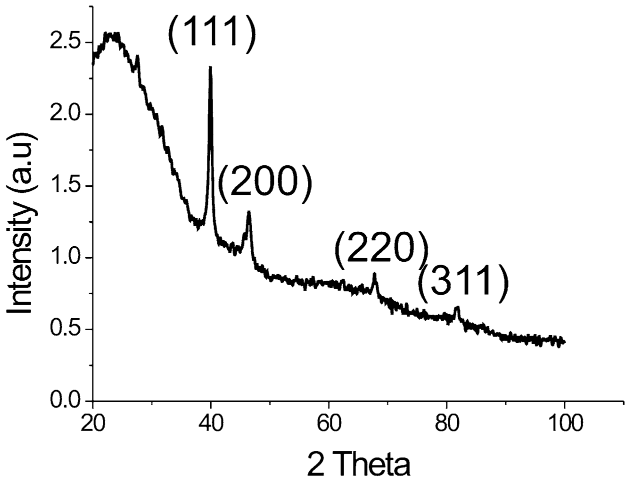

Fig. 3 XRD pattern of colloidal PdNPs synthesized and stabilized with the leaf extract of *C. cainito*

with respect to iodobenzene) and Et_3N as base in aqueous DMF mixture (H_2O:DMF = 3:1) at 115 °C. The progress of the reaction was monitored under UV light as the product is UV active and the complete conversion occurred in 5 h. The product was extracted with diethyl ether and the crude product was purified by column chromatography. The purified product was characterized by NMR spectroscopy.

Reduction reactions

To check the efficacy of the colloidal PdNPs synthesized and stabilized with the leaf extract of *C. cainito* as an effective catalyst for reduction reaction, we have chosen the sodium brorohydride reduction of 3-nitrophenol and 4-nitrophenol in aqueous medium at room temperature as model reactions.

(a) Sodium borohydride reduction of 3-nitrophenol with PdNPs synthesized with the leaf extract of *C. cainito* (100 mg L^{-1})

On treatment of an aqueous solution of 3-nitrophenol with an aqueous solution of freshly prepared sodium borohydride, the absorption maxima at 330 nm was shifted to 390 nm due to formation of more stable 3-nitrophenolate ion which was unchanged for several hours at room temperature. After this observation, a fresh aliquot of 3-NP was charged with freshly prepared $NaBH_4$ in the presence of *C. cainito* leaf extract stabilized colloidal PdNPs (0.1 mL, synthesized with 100 mg L^{-1} leaf extract). Interestingly, complete disappearance of the 3-nitrophenolate ion peak at 391 nm was observed within 30 s with the concomitant formation of a new peak at around 300 nm. This observation demonstrated the excellent catalytic activity of the synthesized colloidal PdNPs from the *C. cainito* leaf extract. Due

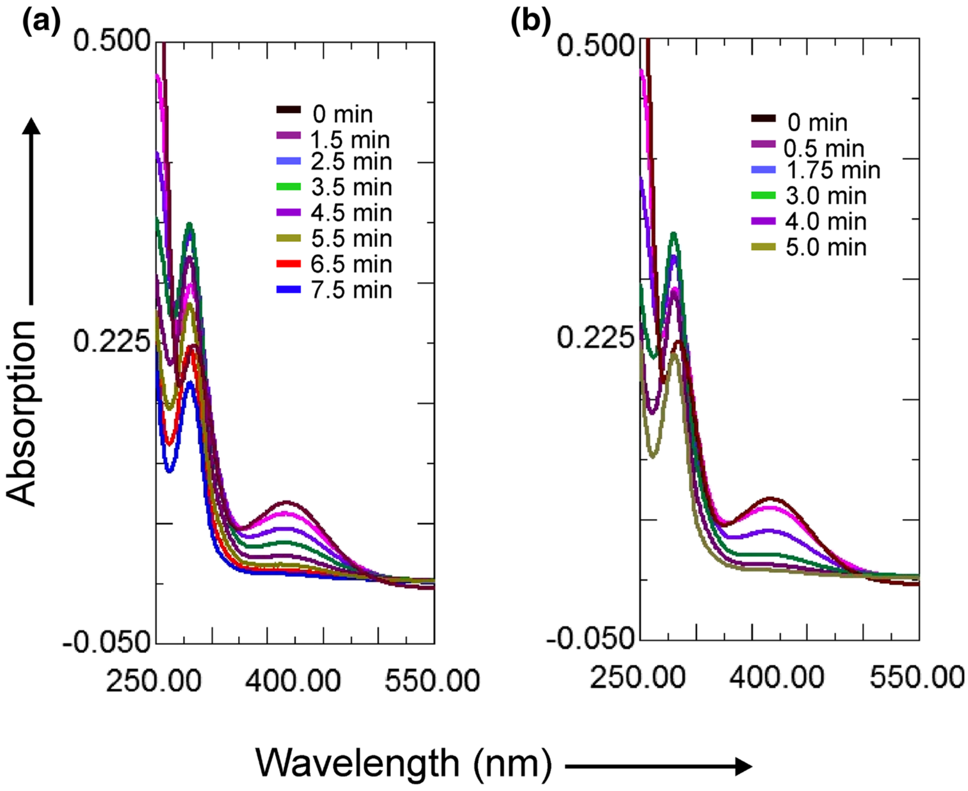

Fig. 4 UV–Visible spectra of the sodium borohydride reduction of 3-nitrophenol to 3-aminophenol at different time intervals in the presence of 0.01 mL colloidal PdNPs as catalyst: **a** colloidal palladium nanoparticles (PdNPs) synthesized and stabilized with 100 mg L^{-1} leaf extract of *C. cainito*; **b** colloidal palladium nanoparticles (PdNPs) synthesized and stabilized with 200 mg L^{-1} leaf extract of *C. cainito*

to the very fast reduction, the value of the catalytic rate constant could not be calculated. For calculating the catalytic rate constant, the volume of the catalyst was reduced to 1/10th (0.01 mL, synthesized with 100 mg L^{-1} leaf extract) in comparison to the previous reaction to slow down the reaction rate. In this case, after the addition of *C. cainito* leaf extract stabilized PdNPs, complete disappearance of the 3-nitrophenolate ion peak was observed within 7.5 min with the concomitant formation of 3-aminophenol at around 300 nm (Fig. 4a). A good linear correlation between $\ln(A_t/A_0)$ vs time was obtained in this case as well and the value of the catalytic rate constant (k) was calculated to be 0.23 min^{-1} (see supporting information Fig. S3).

(b) Sodium borohydride reduction of 3-nitrophenol with PdNPs synthesized with the leaf extract of Star apple (200 mg L^{-1})

Similarly, when a fresh aliquot of 3-NP was charged with freshly prepared $NaBH_4$ in the presence of 200 mg L^{-1} *C. cainito* leaf extract stabilized colloidal PdNPs (0.1 mL), the complete disappearance of the 3-nitrophenolate ion peak at 391 nm was observed within 30 s with the concomitant formation of a new peak at around 300 nm. Then for calculating the catalytic rate constant, the volume of the catalyst was reduced to 1/4th (0.025 mL) to slow down the reaction. Interestingly, on the addition of 1/4th volume of colloidal PdNPs also, the reduction occurred almost instantly and the reaction rate could not be calculated due to very fast reaction. After that, the volume of stabilized PdNPs was further reduced (0.01 mL) to slow down the reaction (0.2 mL 3-nitrophenol + 3.6 mL $NaBH_4$ + 0.19 mL water + 0.01 mL PdNPs). In this case, after the addition of the catalyst, complete disappearance of the 3-nitrophenolate ion peak at 391 nm was observed within 5 min with the concomitant formation of 3-aminophenol at around 300 nm (Fig. 4b). A good linear correlation between $\ln(A_t/A_0)$ vs time was obtained in this case as well and the value of the catalytic rate constant (k) was calculated to be 0.54 min^{-1} (see supporting information Fig. S4).

From the DLS study it is revealed that the hydrodynamic diameters of the PdNPs were in the range of 169.24 nm when the concentration of the leaf extract was 100 mg L^{-1}, whereas the hydrodynamic diameters were decreased to 59.18 nm when the concentration of the leaf extract was 200 mg L^{-1} due to better stabilization of the small-sized PdNPs by the leaf extract. This observation is in agreement with the better efficacy of the colloidal PdNPs synthesized and stabilized with 200 mg L^{-1} *C. cainito* leaf extract than that of the colloidal PdNPs which were synthesized and stabilized with 100 mg L^{-1} *C. cainito* leaf extract because literature study revealed that the smaller size PdNPs posses relatively larger surface to volume ratio which helped the better adsorption of the reactant molecules on the surfaces of the nanoparicles [5]. As a result, very fast hydride transfer occurred from the BH_4^- to the nitrophenolate to reduce it into aminophenolate ion.

(c) Sodium borohydride reduction of 4-nitrophenol with PdNPs synthesized with the leaf extract of Star apple (100 mg L^{-1})

In the similar treatment of aqueous 4-nitrophenol with aqueous $NaBH_4$, the absorption band of 4-nitrophenol at 318 nm was shifted to 401 nm due to the formation of more stable 4-nitrophenolate ion which was unchanged for several hours at room temperature due to the large kinetic barrier of the reaction. After this interesting observation, to check the efficacy of the colloidal PdNPs synthesized and

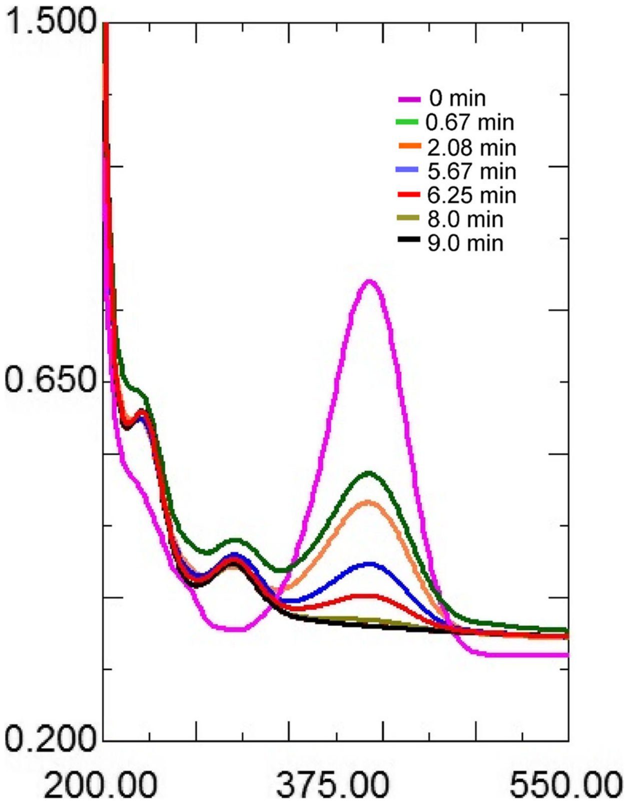

Fig. 5 UV–Visible spectra of the sodium borohydride reduction of 4-nitrophenol to 4-aminophenol at different time intervals in the presence of 0.1 mL colloidal PdNPs synthesized and stabilized with 100 mg L^{-1} leaf of *C. cainito* as catalyst

stabilized with the leaf extract of *C. cainito,* a fresh batch of aqueous 4-NP was charged with freshly prepared aqueous $NaBH_4$ in the presence of colloidal PdNPs (0.1 mL, synthesized with 100 mg L^{-1} leaf extract). The progress of the reaction was monitored by UV–Visible spectrophotometer. The diminishing absorption peak at 401 nm with the certain interval of time and the concomitant formation of a new peak around 300 nm indicated the formation of 4-aminophenolate ion. Complete disappearance of the 400-nm peak was observed within 9 min demonstrating the excellent catalytic activity of the synthesized colloidal PdNPs for the sodium borohydride reduction of 4-nitrophenol at room temperature (Fig. 5). However, the higher reaction rate for the reduction of 3-nitrophenolate than that of the reduction of 4-nitrophenolate is probably due to the higher reactivity of the of the 3-nitrophenolate group than the 4-nitrophenolate.

Conclusions

In summary, we successfully synthesized colloidal palladium nanoparticles (PdNPs) by using medicinally important *C. cainito* leaf extract and $PdCl_2$ solution. The phytochemicals including polyphenolic compounds present in the leaf extract played a crucial role to reduce Pd (II) to Pd (0) and concomitantly stabilize the colloidal PdNPs. The synthesized colloidal PdNPs have shown excellent efficacy as catalyst for Suzuki and Heck coupling reactions under aerobic and phosphine-free conditions in aqueous medium. In addition, the colloidal PdNPs has shown excellent catalytic activity for the sodium borohydride reduction of 3- and 4-nitrophenol also. As the colloidal PdNPs synthesized and stabilized with the leaf extract of *C. cainito* showed excellent catalytic activity for both C–C coupling and reduction reaction, it is evident that the leaf extract of *C. cainito* has played a crucial role as an excellent reducing as well as stabilizing agent to synthesize the surface active PdNPs.

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