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FULL PAPER

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Ultra-low-loading palladium nanoparticles stabilized on nanocrystalline Polyaniline (Pd@PANI): A efficient, green, and recyclable catalyst for the reduction of nitroarenes

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Ultra-low-loading Pd@PANI nanocomposites (0.048 w.t% Pd) were synthesized via a method that combined interfacial polymerization and *in situ* composite with camphor sulfonic acid ((+)-CSA) as a dopant. Transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectra, and X-ray photoelectron spectroscopy (XPS) were performed to characterize the structures. It can be used as an efficient catalyst for the reduction of nitroarenes in aqueous solution by using a smaller amount of $NaBH_4$ (2.5 equiv.) at room temperature with high activity (TON = 3.4×10^3), good stability (cycled eight times), as well as wide applicability (27 substrates). The catalyst also showed a marvelous activity in the gram-level reaction (yield = 92%). UV–Visible spectrophotometry was used to investigate the reaction kinetics for the reduction of 4-nitrophenol to 4-aminophenol, and the results reconfirmed the excellent performance of the catalyst. The unique properties and superior performance of the prepared ultra-low-loading Pd@PANI nanocomposites lead it be an attractive alternative catalyst for conventional organic catalytic applications.

KEYWORDS
catalytic performance, palladium nanoparticle, polyaniline, reduction of nitroarenes in water, reused for multiple cycles

1 | INTRODUCTION

Polyaniline (PANI) is considered to be one of the most promising multifunctional polymers due to its easy preparation, high electrical conductivity, good performance for supported catalytic materials, excellent environmental stability, and low cost.[1–7] Moreover, metal/PANI composites have been applied in organic reactions in a significant way,[8–22] which are extremely cheap and recyclable in comparison with organometallic complexes.[23]

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Among nano-M@PANIs, nano-Pd@PANI is one of the most important catalysts due to its wide catalytic applications in various organic reactions.[24–29] The preparation of nano-Pd@PANI is usually based on the initial oxidation of aniline monomers to obtain PANI carriers. Then, the nanoparticles are obtained by impregnating with Pd.[28] It is worth noting that the Yu et al. research team[24–26,30] recently reported the catalyst obtained by oxidizing aniline via air or hydrogen peroxide and showed an ultra-low metal load (0.12–0.75%) and high stability. The catalyst has been successfully applied for Suzuki cross-coupling[24,31] with a high turnover number (TON) at 4.7 × 10^3, which showed the possibility of utilizing ultra-low supported catalyst materials.

Of late, more and more studies on metal NPs supported on a recyclable polymer-supported palladium catalyst,[32–36] such as graphene oxide[37,38] or graphene,[39] have been reported for the reduction of nitroarenes. However, the nano-M@PANIs materials are not widely accepted for the reduction of nitroarenes, since the reactions require to use of excessive amounts of $NaBH_4$ and additional organic auxiliaries.[40] Moreover, using large amounts of metal as a catalyst leads to heavy-metal contamination and very low TON values.[41–44] Hence, an alternative, cost-effective, high-activity, high-stability, and more environmentally friendly reduction of nitroarenes with negligible metal contamination is of high demand.[45]

Herein, we designed and synthesized a well-dispersed Pd@PANI catalyst via self-stabilized dispersion polymerization (SSDP) method by using camphor sulfonic acid ((+)-CSA) as a dopant. The dark golden powder was obtained in 75% yield (Figure 1a). Inductively coupled plasma mass spectrometry (ICP-MS) analysis indicated that the weight ratio of Pd NPs in the material was 0.0476%. After a series of conditions optimizations, the Pd@PANI catalyst was successfully applied to reduce various nitroaromatics with water as the solvent and could be reused for more than eight times without deactivation, indicating great potential for reagent development. The reaction kinetics were also studied in our work.

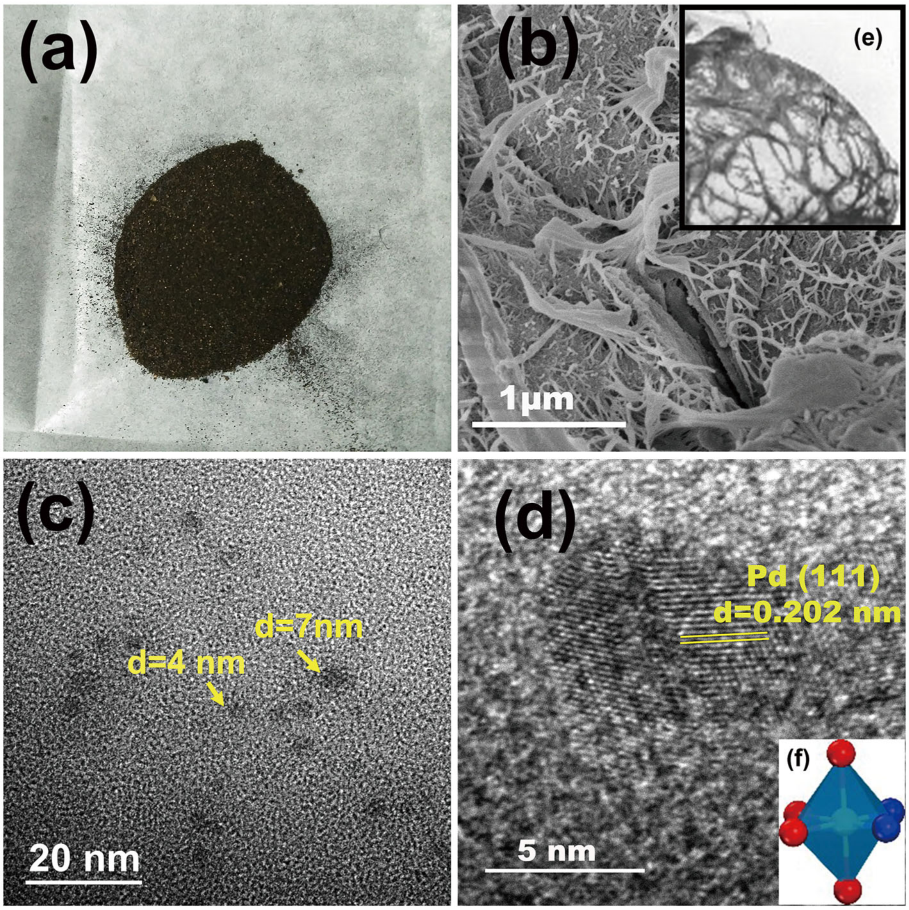


FIGURE 1 (a) Photograph of the Pd@PANI catalyst. (b) Scanning electron microscope (SEM) image of Pd@PANI catalyst. (c–d) HRTEM image of Pd@PANI catalyst (Pd NPs: small black dots)

2 | EXPERIMENTAL

2.1 | General methods

All reagents are more than 98% pure and the solvent is A. R. It is used directly after purchase. Unless otherwise stated, the reaction is carried out in air. ^{1}H and ^{13}C NMR were recorded by Bruker 400 MHz spectrometer. ICP-MS measurements were conducted by Agilent 7800. The morphology of the materials was obtained on JEOL JEM-2010F High Resolution Transmission Electron Microscope (HRTEM). The powder X-ray diffraction (XRD) patterns were recorded by a D/max 2200 PC03030502 X-ray diffractometer using Cu-Karadiation. Fourier transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm^{-1} using a Spectrum Two03040404 FT-IR spectrometer. The X-ray photoemission (XPS) spectra were performed at room temperature using a Thermo ESCALAB 250xi hemispherical electron energy analyzer.

2.2 | Gram-scale preparation of Pd@PANI

Aniline (1.864 g, 20 mmol), camphor sulfonic acid (4.686 g, 20 mmol), deionized water (40 ml), and chloroform (50 ml) were added to a jacket reactor. Mechanical stirring was applied and cooling lowered the temperature to −35 °C until the solution was a white paste. Then $PdCl_2$ (89.29 mg, 0.5 mmol), $(NH_4)_2S_20_8$ (4.564 g, 20 mmol), and camphor sulfonic acid (20 mmol) were added to the reactor. Continuous stirring continued until the solution was completely blue-black, and static inversion was carried out at a low temperature (−35 °C). The blue-black Pd@PANI was obtained by filtration, washing with deionized water for four times and ethanol for four times, using 1 mol/L sodium hydroxide (50 ml) for the acid removal treatment, washing with water and ethanol to neutral pH conditions, and then vacuum drying at 60 °C for 4 hr for collection and use.

2.3 | General procedure for the reduction reaction

Nitrobenzene (0.5 mmol), sodium borohydride (1.25 mmol), and 0.03 g Pd@PANI (1.4×10^{-2} mg of calculated palladium) were added into a 25 ml reaction bottle, and 2 mL of deionized water was added and stirred at room temperature. TLC followed up the reaction. After the reaction, the catalyst was collected by centrifugalizing and was reused in the next round of reactions. The organic phase was washed with saturated salt water and dried with anhydrous Na_2SO_4. The product was separated and purified by silica gel column chromatography. The structure of the product was characterized by proton nuclear magnetic resonance (^{1}HNMR) and carbon-13 nuclear magnetic resonance (^{13}CNMR). Characterization data of the products are given in the Supplementary Material.

2.4 | General methods: Ultraviolet spectrophotometric determination of reduction reaction of 4-Nitrophenol

4-nitrophenol (2.6×10^{-4} mol) and sodium borohydride (0.13 mol) were added to a 250 mL flask. Then, 100 ml of deionized water was added and stirred for 30 min at room temperature under the argon atmosphere. Accurately remove 2 ml of solution from the reaction and dilute to 100 ml, and the full wavelength absorbance was measured by a ultraviolet (UV–Vis) spectrophotometer, with the result was recorded as 0 min. Pd@PANI catalyst (30 mg) was added to the reaction bottle, and the above operation was repeated at certain time intervals. The full wavelength absorbance determination was carried out by a UV–Vis spectrophotometer.

2.5 | TON and TOF value calculation method in Table 2

$$\mathrm{TON} = \frac{\text{Number of moles of reactant conversion}}{\text{moles of catalyst active centers}} = \frac{\mathrm{D*Y}}{\mathrm{B}} \qquad \left(B = \frac{m*C}{M}\right) \tag{1}$$

$$\mathrm{TOF} = \frac{\text{Reaction time}}{\mathrm{TON}} \tag{2}$$

TON is the turnover number, indicating the molar amount of reactants converted per unit of active site (Equation (1)). "D" represents the mole fraction of the reactants added (mmol), "Y" represents the conversion rate of the reactants, "m" represents the mass of the catalyst added in the reaction (mg), "C" represents the percentage of active sites contained in the catalyst (In this paper, the active center of the catalyst is approximately equal to the Pd content obtained by ICP test), "M" represents the mass fraction of metal palladium. TOF is the turnover frequency, represents the amount of reactant that is converted per unit time by the unit active site (Equation (2)).[31,46]

3 | RESULTS AND DISCUSSION

3.1 | Crystal structure and morphology of catalyst

The catalysts loaded with Pd always show excellent catalytic performance for reduction reactions, but their high price limits their application. Therefore, it is necessary to develop a supported Pd catalyst with low Pd loads and appreciable activity compared with conventional catalysts. Recently, our research team synthesized ultra-low-loading Pd@PANI nanocomposites by the combination of interfacial polymerization and in situ composite method. An aqueous solution of camphor sulfonic acid ((+)-CSA) and $PdCl_2$ were used as raw materials and ammonium peroxodisulfate as the oxidant during the preparation.[28] The *in situ* doping and loading were completed in about 4 hr by a one-pot method. Then, the CSA-doped polyaniline nanoparticles were deacid-doped by NaOH aqueous solution (1 M). After the CSA was completely removed, a black Pd@PANI nanocomposites without CSA was finally obtained. Compared with the Pd nanoparticles grown by combining aqueous nanofiber dispersion with a solution of palladium (II) nitrate (4:1) and incubation for 1 d,[28] and the air stirring of $PdCl_2$ and aniline for 96 hr,[24] the reaction time was greatly reduced in this work. Moreover, this method eliminated the need for a separate reduction step. Fortunately, the black Pd@PANI nanocomposites are quickly obtained in the air rather than brown (Figure 1, Image a).[31] Additionally, the successful preparation strategy of ultra-low-loading Pd catalysts on Pd@PANI nanoparticles has the advantage of using much less Pd than traditional catalysts (currently only 0.048% Pd vs. previously 0.125–0.75%[31] and 10.0%[24] Pd).

Figure 1 (b) shows a scanning electron microscope (SEM) image of the Pd@PANI catalyst. The fiber net of Pd@PANI, like arachnoids in the brain, can be observed in the image. This is different from the lamellar polyaniline prepared by the conventional method. The use of camphorsulfonic acid in the polymerization of aniline can effectively adjust the growth of polyaniline, and linearly grow to obtain a linear network of polyaniline material. Besides, linear mesh structures may also be one of the reasons for the extremely low metal loading. The transmission electron micrograph (TEM) images of the Pd@PANI indicate the Pd nanoparticles have good dispersion on the PANI support (Figure 1, Image c), and the average size of the Pd nanoparticles was determined to be in the range of 4–7 nm. High-resolution transmission electron microscopy (HR-TEM, Figure 1, Image d) shows Pd (111) lattice planes with a spacing of d(111) = 0.223 nm, consistent with the literature value for nanocrystalline Pd,[26,31] Therefore, it was thought that the coordinate structure of Pd and polyaniline is an asymmetric octahedron (Figure 1(e)). Octahedral nanocrystals (Pd (111)) and structures have the highest surface energy in the

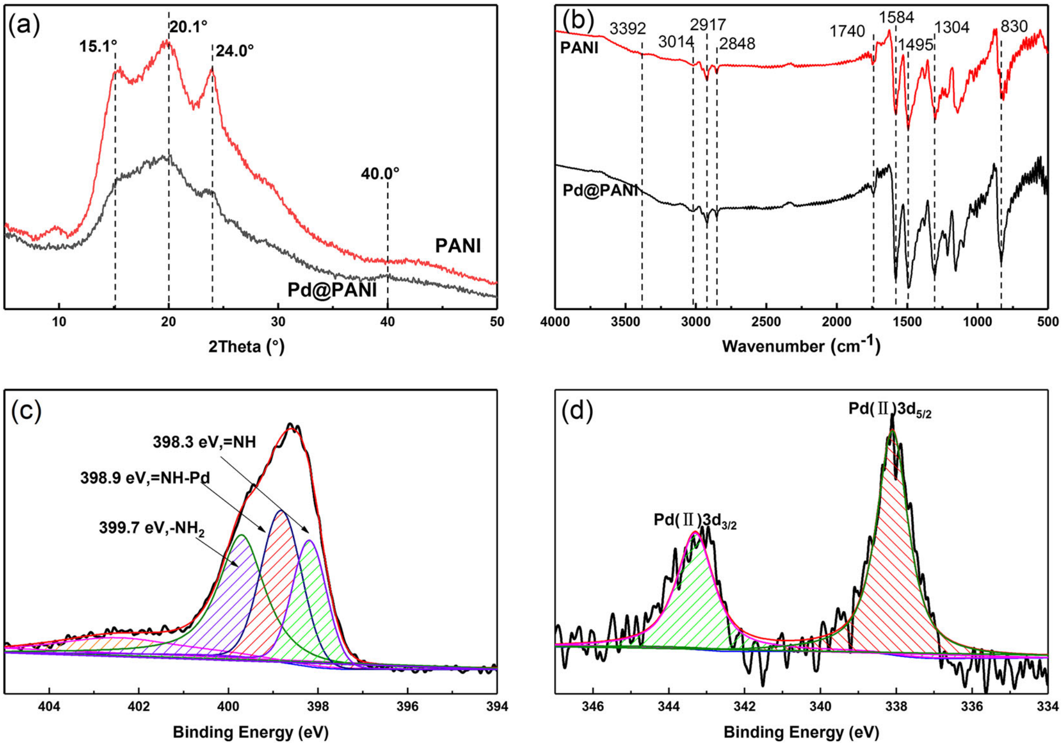


FIGURE 2 (a) XRD of the Pd@PANI; (b) IR of the Pd@PANI; (c) XPS N 1 s of the Pd@PANI; (d) XPS Pd 3d of the Pd@PANI

presence of reductant and are highly active to the reduction of nitrobenzene by $NaBH_4$.

3.2 | Catalyst characterization

The crystalline structures of the Pd@PANI catalyst were characterized by X-ray diffraction (XRD), shown in Figure 2(a). XRD patterns of PANI and Pd@PANI revealed that the polyaniline salt was partially crystalline and shows peaks at $2\theta = 15.1$, 20.1, and 24.0 corresponding to the interface distances (d) of 6.1, 4.3, and 3.5 Å,[36,47] respectively. However, a new diffraction peak appears at 40° (Pd (111)) in the curve of Pd@PANI, which belongs to the amorphous diffraction peak of Pd. It is also observed that the regularity of Pd@PANI is lower than PANI, because Pd inserts into the space between PANI chains. From ICP-MS we can find the load of the precious metals of the Pd@PANI catalyst is much lower than that of the materials prepared through the aerobic oxidation method (10.0%)[24,26] or interfacial emulsion polymerization only by ammonium persulfate oxidation.[22] It is also significantly lower than the materials prepared by hydrogen peroxide oxidation (0.75%).[31]

The molecular structure of the Pd@PANI net was characterized by Fourier-transform infrared spectroscopy (FTIR) (Figure 2b), which shows the characteristic peaks of PANI at 1584 and 1495 cm^{-1} (quinoid and benzenoid ring, respectively)[26]; the ratio of quinoid and benzenoid is determined to be ca 16:31. In addition, there is no characteristic peak of CSA (C=O 1730 cm^{-1}, S=O 1160 cm^{-1}, C-S 752 cm^{-1}) in the infrared spectrum. It shows that CSA has been completely removed after dedoping with sodium hydroxide, which does not affect the catalytic activity in the subsequent reaction. Camphor sulfonic acid acts as a templating agent in the preparation process. It essentially acts to regulate the molecular morphology and size of polyaniline.

XPS results showed that only Pd^{2+} existed in the fresh material. The XPS spectrum of N is deconvoluted into three major component peaks centered at 399.7($-NH_2$), 398.9, and 398.3(=NH) eV, and the linewidths are 1.1, 0.85, and 0.74 eV, respectively, in Figure 2 (c) and (d). The binding energy of 398.9 eV suggests that the quinoid ring of PANI is adsorbed (combined) with the plane of the ring parallel to the metal surface of Pd (111), with the bonding being via the π orbitals of quinoid ring or imine in the PANI and the lone-pair on the N atom.[24] Additionally, for Pd spectra, two major component peaks centered at 343.3($3d_{3/2}$) and 338.1($3d_{5/2}$) eV with linewidths of 1.17 eV and 1.0 eV, respectively, which are attributed to a divalent palladium structure.

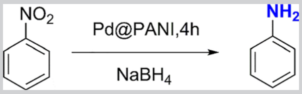
3.3 | Reduction of nitroarenes by Pd@PANI

The initial conditions of the reaction are: catalyst 50 mg, four equivalents of sodium borohydride, 100 °C, using water as a solvent, and the yield detected by ^{1}HNMR with 1,3,5-trimethoxybenzene as the internal standard. To our great delight, when using 30 mg Pd@PANI catalyst to catalyze the hydrogenation of 0.5 mmol of nitrobenzene with 2 mmol of $NaBH_4$ in H_2O, 92% yield of aniline is obtained in 4 hr (Table 1, entry 3, 7). Too much or little catalyst leads to a decrease of yield, which may be related to the course of the reaction. Different amounts of catalyst have different controls of the intermediate path of the reaction, and the by-products involved are different (Table 1, entries 1–4). It is interesting to note that the best yield can be obtained with 2.5 equivalents of sodium borohydride (entry 7). When the sodium borohydride is less than two equivalents, the nitrobenzene cannot be completely reduced, and a large amount of nitrogen oxybenzene by-product is produced (entries 8–9). Next, we tried different reducing agents, such as hydrazine hydrate (entry 10), ascorbic acid (entry 11) and formate (entry 12), but did not get good results. This may be because the reducing mechanism of different reducing agents is different, and a reducing agent such as formate amine can be decomposed under the action of a catalyst to generate hydrogen in situ. Sodium borohydride is a nucleophilic addition of the positive charge center by the dissociated hydrogen anion. The reaction does not require heating and have a higher yield at room temperature (entry 16). Finally, by comparing the activities of the reactions in different solvents, it was found that the catalysts gave good results in methanol, ethanol, trifluoroethanol, and hexafluoroisopropanol (entries 17–21). It was also confirmed that sodium borohydride does not reduce nitrobenzene without the addition of a catalyst (entry 23). After an optimization of the conditions and taking into account the energy-saving and environmentally friendly green chemical production concept, it can be concluded that the optimum reaction conditions are 30 mg of catalyst, 2.5 equivalents of sodium borohydride, at room temperature in water, with a 92% yield of aniline obtained in 4 hr.

Most impressively, the ultra-low-loading palladium loading nanoparticle (Pd@PANI) can be reused by simple centrifugation and shows excellent stability and recyclability (Table 1, entry 16$^{e–h}$). Notably, this catalyst could be used for 20 mmol-scale without the product yield decreasing (entry 22), showing good practicability for organic synthesis.

We are pleased that the catalyst has broad applicability in the nitro reduction reaction. Whether the substituent is an electron donating group or an electron withdrawing group,

TABLE 1 Optimization of reaction conditions[a]



Entry	Pd@PANI (mg)	Hydrogen source (equiv.)	Temp (°C)	Solvent	Yield[b] (%)
1	50	$NaBH_4$ (4)	100	Water	82
2	40	$NaBH_4$ (4)	100	Water	74
3	30	$NaBH_4$ (4)	100	Water	92
4	20	$NaBH_4$ (4)	100	Water	82
5	30	$NaBH_4$ (3.5)	100	Water	74
6	30	$NaBH_4$ (3)	100	Water	76
7	30	$NaBH_4$ (2.5)	100	Water	92
8	30	$NaBH_4$ (2)	100	Water	76
9	30	$NaBH_4$ (1.25)	100	Water	56
10	30	$NH_2.NH_2$ H_2O (4)	100	Water	N.R[c]
11	30	Vitamin C (4)	100	Water	Trance[d]
12	30	$CHOONH_4$ (4)	100	CH_3OH	10
13	30	$NaBH_4$ (2.5)	80	Water	81
14	30	$NaBH_4$ (2.5)	60	Water	85
15	30	$NaBH_4$ (2.5)	40	Water	87
16	30	$NaBH_4$ (2.5)	R.T	Water	92,90[e],91[f],93[g],91[h]
17	30	$NaBH_4$ (2.5)	R.T	MeOH	94
18	30	$NaBH_4$ (2.5)	R.T	EtOH	90
19	30	$NaBH_4$ (2.5)	R.T	i-PrOH	N.R[c]
20	30	$NaBH_4$ (2.5)	R.T	TFE	89
21	30	$NaBH_4$ (2.5)	R.T	HFLP	92
22	1200	$NaBH_4$ (2.5)	R.T	Water	92[f]
23	/	$NaBH_4$ (2.5)	R.T	Water	/

[a] Nitrobenzene (51 μL, 62 mg, 0.5 mmol), 2 ml water, stir at room temperature for 4 h.

[b] The yield detected by^{1}HNMR with1,3,5-Trimethoxybenzene as internal standard.

[c] No reaction product detected.

[d] Yield <3%.

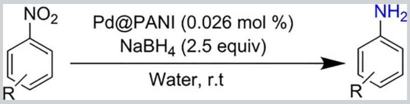
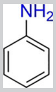
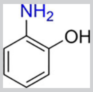
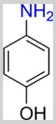
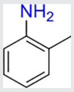
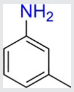
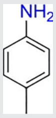
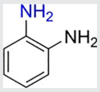
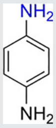
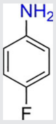
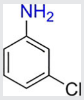
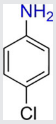
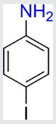
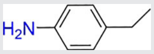
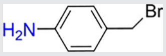
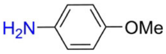
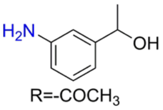
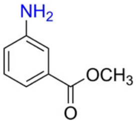
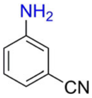
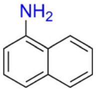
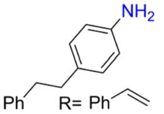
[e] Conversion of nitrobenzene with the reusability of catalyst.

[f] Reaction scale enlarged to 20 mmol, isolated yield.

we can obtain a high yield. After 360 minutes of reaction, the reduction product aniline of nitrobenzene was obtained in a yield of 92% (Table 2, entry 2a). When the substituent group is a hydroxyl group, the reaction time is the shortest, and the 2-, 3-, 4-substituted product can be obtained in 30 minutes. At the same time, we can find that when the substituent group is 3-substituted, it can get higher yield in a shorter time (Table 2, entries 2c, 2f). When the substituent group is a halogen element (Table 2, entries 2j–2n), the reactivity of the fluorine atom is the strongest, which may be related to the electronegativity of the atom. The fluorine atom has strong electronegativity and strong electron-withdrawing ability, which makes the electron cloud density on the entire benzene ring lower, which is more conducive to the reduction reaction.

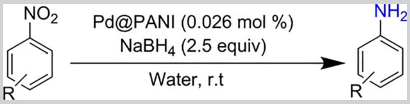
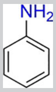
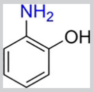
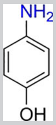
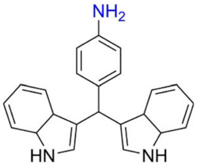
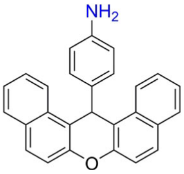
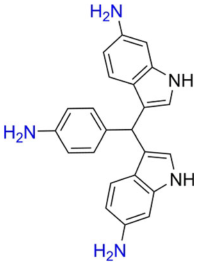
Interestingly, nitrobenzenes containing carbonyl groups on the benzene ring are reduced at the same time (Table 2, entries 2r–2 s). Similarly, styrene-substituted nitrobenzene, carbon–carbon double bonds, and nitro groups are also present (Table 2, entries 2x), but halogenated nitrobenzene and cyano-substituted nitrobenzene are reduced only by a nitro group (Table 2, entries 2j–2n, 2u). It is worth noting that the yield of the compound containing three nitro groups, nitro-containing bisindole methane derivatives and the heterocyclic are high (Table 2, entries 2y–3a, 2z), while $NaBH_4$ dosage was half

TABLE 2 Scope of substrates catalyzed by Pd@PANI[a,b]

 			
			
2a, 4 h, 92%[c] **TON = 3.4×10^3** **TOF = 11×10^{-4} h^{-1}**	**2b, 0.25 h, 96%** [d] **TON = 3.5×10^3** **TOF = 0.7×10^{-4} h^{-1}**	**2c, 0.08 h, 97%** [d] **TON = 3.6×10^3** **TOF = 0.2×10^{-4} h^{-1}**	**2d, 0.41 h, 92%** [d] **TON = 3.4×10^3** **TOF = 1.2×10^{-4} h^{-1}**
			
2e, 1.5 h, 88% **TON = 3.3×10^3** **TOF = 4.5×10^{-4} h^{-1}**	**2f, 1.5 h, 88%** **TON = 3.3×10^3** **TOF = 4.5×10^{-4} h^{-1}**	**2 g, 1.5 h, 90%** **TON = 3.3×10^3** **TOF = 4.4×10^{-4} h^{-1}**	**2 h, 0.66 h, 61%** **TON = 2.2×10^3** **TOF = 2.9×10^{-4} h^{-1}**
			
2i, 0.66 h, 90% **TON = 3.3×10^3** **TOF = 1.9×10^{-4} h^{-1}**	**2j, 0.5 h, 95%** [e] **TON = 3.5×10^3** **TOF = 1.4×10^{-4} h^{-1}**	**2 k, 0.66 h, 85%** **TON = 3.1×10^3** **TOF = 1.9×10^{-4} h^{-1}**	**2 l, 0.33 h, 42%** **TON = 1.5×10^3** **TOF = 2.1×10^{-4} h^{-1}**
			
2 m, 1 h, 34% **TON = 1.2×10^3** **TOF = 7.9×10^{-4} h^{-1}**	**2n, 3 h, 80%** **TON = 2.9×10^3** **TOF = 10×10^{-4} h^{-1}**	**2o, 1.5 h, 88%** **TON = 3.2×10^3** **TOF = 4.5×10^{-4} h^{-1}**	**2p, 4 h, 61%** **TON = 2.2×10^3** **TOF = 17×10^{-4} h^{-1}**
	 	 	
2q, 6 h, 92% **TON = 3.4×10^3** **TOF = 17×10^{-4} h^{-1}**	**2r, 2 h, 63%** **TON = 2.3×10^3** **TOF = 8.5×10^{-4} h^{-1}**	**2 s, 4 h, 61%** **TON = 2.2×10^3** **TOF = 17×10^{-4} h^{-1}**	**2 t, 2 h, 64%** **TON = 2.4×10^3** **TOF = 8.3×10^{-4} h^{-1}**
			
2u, 2 h, 63% **TON = 2.3×10^3** **TOF = 8.5×10^{-4} h^{-1}**	**2v, 3.5 h, 44%** **TON = 1.6×10^3** **TOF = 21×10^{-4} h^{-1}**	**2w, 2 h, 74%** **TON = 2.7×10^3** **TOF = 7.2×10^{-4} h^{-1}**	**2x, 1 h, 74%** [f] **TON = 2.7×10^3** **TOF = 3.6×10^{-4} h^{-1}**

(Continues)

TABLE 2 (Continued)

 			
			
			
2y, 2 h, 82% [f] **TON = 3.0×10^3** **TOF = 6.5×10^{-4} h^{-1}**	**2z, 2 h, 90%** [f] **TON = 3.3 ×** **10^3 TOF = 5.9×10^{-4} h^{-1}**	**3a, 5 h, 70%** [f, g] **TON = 2.6×10^3** **TOF = 19×10^{-4} h^{-1}**	

Reaction Conditions:

[a] Reaction Conditions: nitroarene (1 mmol), $NaBH_4$ (1.25 mmol), Pd@PANI (0.026 mol %), distilled water (2 mL), room temperature.

[b] Isolated yields.

[c] Yield detected by ^1H NMR with Dibromomethane as internal standard.

[d] Yield after work up.

[e] 24% of 3-Methoxyaniline.

[f] Reaction at 100 °C.

[g] 5 equivalents of $NaBH_4$ was used.

of normal. Therefore, polyaniline is not only a supporting material for metals, but also acts as a nitrogen-containing ligand to synergistically increase the activity of the catalyst. The catalyst was tolerant to nitrogen and oxygen and the reactions of 1y and 1z afforded the desired products 2y in 82% yield and 2z in 90% yield. Thus, the ability of the Pd@PANI for nitrobenzene reduction with a high TON value is an order of magnitude higher than other novel divalent catalysts reported recently for the reduction of nitrobenzene. Additionally, 1.4 g of the catalyst can be produced in a single batch, which has a higher value than the catalyst of micro-preparation for application.

3.4 | Recycle and reuse of the catalyst

In addition, we examined the reusability of the catalyst. After each reaction, the catalyst was collected by simple filtration, washed several times with water and ethanol, dried in a vacuum oven and placed in the next use. We found that the catalyst was used 8 times, the activity was not reduced, and the yield was 93% (Figure 3a).

After repeated use of the catalyst for six times, the original reticular fiber structure was destroyed, and some fibers appeared agglomerated, but the obvious pore structure was still observed in the material (Figure 3b). It can be seen from Figure 3c that the crystal form of polyaniline changes after the catalyst is used six times, but a distinct diffraction peak of palladium can be seen at 40.0°. In addition, we found in the infrared spectrum that the catalyst used 6 times showed significant blue-shifting at 1377 and 830 cm^{-1}, peak positions moved from 1377 and 830 cm^{-1} to 1282 and 807 cm^{-1}, respectively.

Figure 3e shows the N 1 s XPS core-level spectra of Pd@PANI net catalyst that was already used six times. The spectrum of N is deconvoluted into three major component peaks centered at 400.1, 399.5(-NH_2), and 398.3(=NH) eV, and the linewidths are 1.18, 0.90, and 0.92 eV, respectively. However, binding energies at 400.1 shows that the nitrogen atoms of amino coordinated to Pd(0)[25] via the lone-pair on the N atom of the amino without any π orbitals, consistent with the rules of XPS chemical shift.[26] Figure 3f shows the Pd 3d XPS core-level spectra of a Pd@PANI net catalyst that was already used six times. The ratio of divalent Pd (342.3 eV $3d_{3/2}$, 337.1 eV $3d_{5/2}$) to zero-valent Pd (341.1 eV $3d_{3/2}$, 335.8 eV $3d_{5/2}$) is 1:2, indicating that

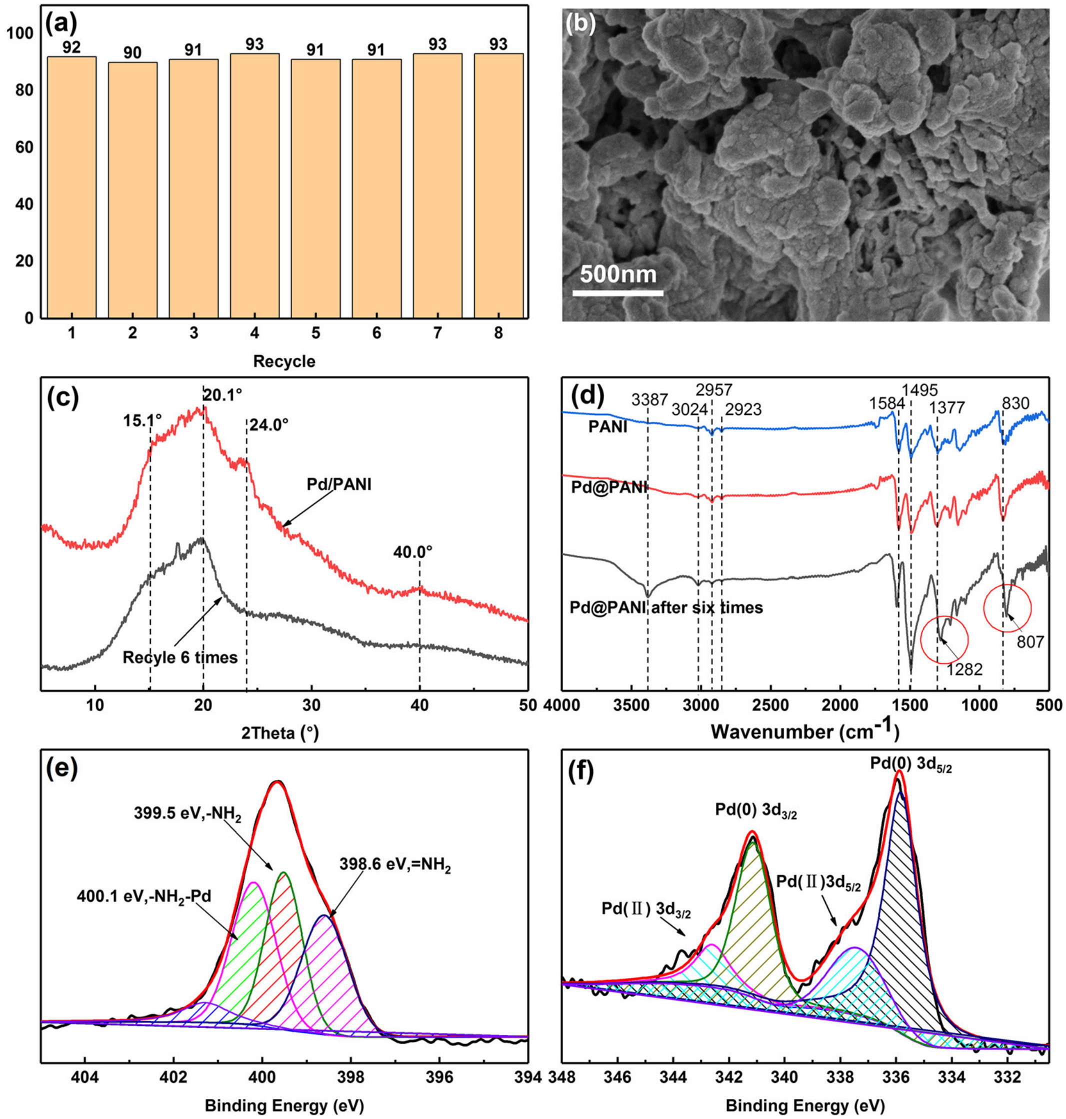


FIGURE 3 (a) Recycle and reuse of the Pd@PANI catalyst; (b) SEM of Pd@PANI catalyst after recycling six times; (c) XRD pattern of 6-recycled Pd@PANI; (d) FT-IR spectra of PANI, Pd@PANI catalyst and after six times; (e) and (f) XPS spectra of 6-recycled Pd@PANI

most of the divalent palladium has been reduced to zero-valent palladium by sodium borohydride during reaction. Pd^0 should be the real catalytic species generated via the reduction of Pd^{2+} by sodium borohydride.[26,31] Although morphology (Figure 3b), crystal structure (Figure 3c) and the valency of Pd has been changed after reaction, the yield after eight repeated cycles is very excellent (93%).

3.5 | The kinetics of the reduction of nitroarenes by Pd@PANI

We investigated the kinetics of our developed catalyst for the reduction reaction by using 4-nitrophenol as a model substrate. The apparent rate constant of 4-nitrophenol reduction was calculated by performing a full wavelength scan using an ultraviolet–visible spectrophotometer, and the activity of the catalyst was further compared. Usually, the aqueous solution of 4-nitrophenol exhibits a maximum absorption peak at 317 nm,[48] but after the addition of the reducing agent sodium borohydride, the maximum absorption peak is red-shifted to 400 nm.[49] It can be seen from the figure that after the addition of the Pd@PANI catalyst to the reaction mixture, the maximum absorption peak at 400 nm immediately decreases, and at the same time, a new peak appears at 300 nm due to the formation of the reduction product 4-aminophenol.

It can be noticed that the reaction was carried out immediately after the addition of the catalyst, and there was no induction time (Figure 4a and 4c). This was because we introduced argon into the solution before the start of the reaction, the effect of dissolved oxygen in the water on the reaction was excluded. Secondly, the

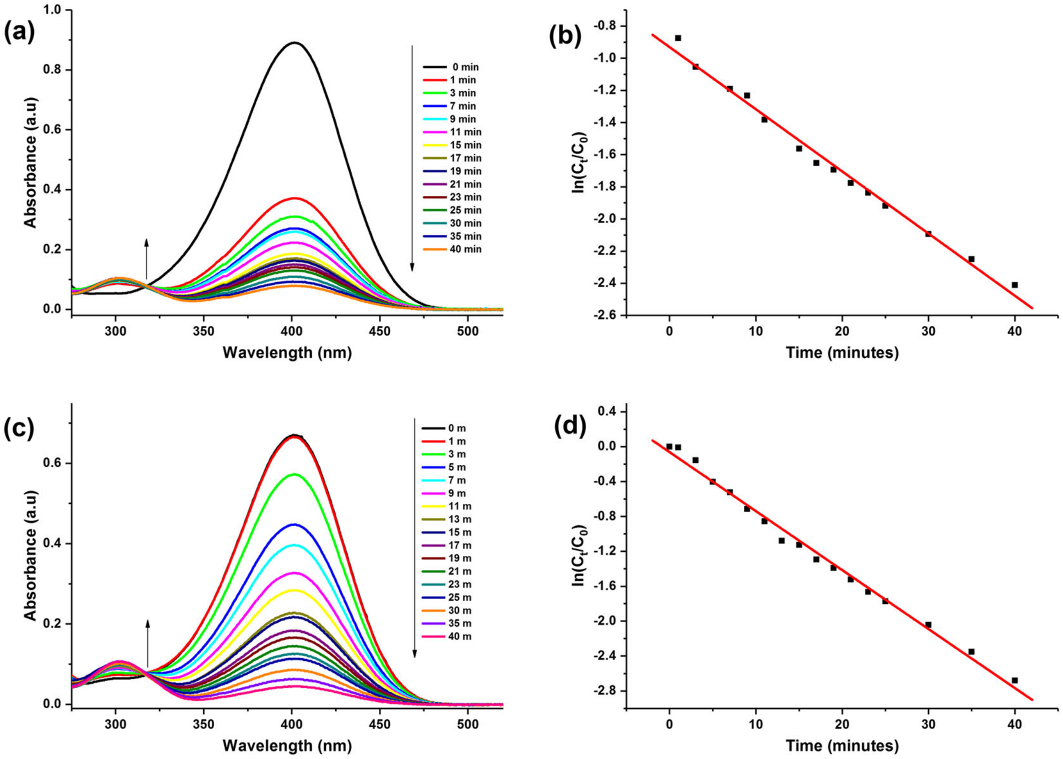


FIGURE 4 (a, c) Successive UV–visible spectra of 4-nitrophenol using: (a) First use, (c) Repeated six times catalysts. (b, d) Plot of ln (C_t/C_0) versus time for the reduction of 4-nitrophenol with (b) First use, (d) Repeated six times catalyst

reducing agent sodium borohydride is in absolute excess, so pseudo-first-order kinetic assumptions can be applied to the 4-nitrophenol alone (Equation (3)).[50,51] A_0 is the absorbance at time 0, A_t is the absorbance at time t, and Kapp is the apparent rate constant for reaction.

$$\frac{dC_t}{dt} = -K_{app}C_t \quad \text{or} \quad -\frac{\ln C_t}{C_0} = -K_{app}t \quad \text{or} \quad -\frac{\ln A_t}{A_0} = -K_{app}t \tag{3}$$

Figure 4 shows the Plot of ln (C_t/C_0) versus time for the reduction of 4-nitrophenol with (Figure 4b) First use, (Figure 4d) Repeated six times catalyst. From the slope of the line obtained by plotting $\ln C_t/C_0$ vs. time, the apparent rate constant (K_{app}) for the reduction of 4-nitrophenol could be obtained. For the first-used catalyst, K_{app} was found to be 6.4×10^{-4} s^{-1}. Repeated six times, K_{app} was found to be 11.2×10^{-4} s^{-1}. A comparison of the K_{app} values has been provided in Table 3. We found that the catalyst cycled for six times had approximately twice the apparent reaction rate constant (K_{app}) than fresh catalyst. This means that the efficiency of the catalyst enhances while the reaction proceeds, and the ability of Pd(0) is higher than Pd (II) in the Metal/PANI system (Table 3).

TABLE 3 Comparison of K_{app} with different usage times catalysts for the reduction of 4-nitrophenol

Catalyst	K_{app} ($\times 10^{-4}$ s^{-1})	Error limits
First use	6.4	± 0.0108
Repeated six times	11.2	± 0.0089
$PdCl_2$	9.8	± 0.0019
PS@PANI@Au/m-SiO_2	8.3	R. f[20]

4 | CONCLUSIONS

In conclusion, a Pd@PANI net containing 0.046 w.t.% Pd was prepared in situ by a simple protocol at a gram-scale and was characterized by XRD, XPS and TEM techniques. Palladium nanoparticles with a size of about 4–7 nm were uniformly dispersed on PANI without significant agglomeration. Compared with previously reported catalytic systems, the Pd@PANI nanoparticles have the following three advantages: (i) The catalyst can reduce nitroaromatic hydrocarbons to corresponding aminoaromatic hydrocarbons in aqueous solution at room temperature only using $NaBH_4$ (2 equiv.) as a hydrogen source; (ii) The catalyst has high stability and can be recycled more than eight times. (iii) The ultra-low-loading Palladium and higher TON value (TON = 3.4×10^3).

The unique properties of this catalyst make it an attractive alternative for conventional organic catalytic applications. More related works are ongoing in our laboratory to develop the practical green synthetic methodologies.

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