Recyclable nanocellulose-confined palladium nanoparticles with enhanced room-temperature catalytic activity and chemoselectivity

Juan Meng[†], Yongzhuang Liu[†], Xiaochao Shi, Wenshuai Chen, Xianquan Zhang^{*} and Haipeng Yu^{*}

ABSTRACT We describe the synthesis of even-dispersed palladium nanoparticles (Pd NPs) confined within a cellulose nanofiber (CNF) matrix for developing a high-performance and recyclable catalyst. The CNF matrix was composed of CNF-assembled mesoporous nanosheets and appeared as soft and hydrophilic foam. Ultrafine Pd NPs (~6 nm) with high-loading (9.6 wt%) were *in situ* grown on these mesoporous nanosheets, and their dense spatial distributions were likely to generate nano-confinement catalytic effects on the reactants. Consequently, the CNF-confined Pd NPs (CNF-Pd) exhibited an enhanced room-temperature catalytic activity on the model reaction of 4-nitrophenol hydrogenation with a highest rate constant of $8.8 \times 10^{-3} \text{ s}^{-1}$ and turnover frequency of 2640 h^{-1} . The CNF-Pd catalyst possessed good chemical stability and recyclability in aqueous media which could be reused for at least six cycles without losing activity. Moreover, chemoselective reduction of 3-nitrostyrene was achieved with high yield (80%–98%) of 3-aminostyrene in alcohol/water co-solvent. Overall, this work demonstrates a positive nano-confinement effect of CNFs for developing stable and recyclable metal NP catalysts.

Keywords: nanocellulose, deep eutectic solvents, palladium nanoparticles, catalysts, nano-confinement

INTRODUCTION

Metal nanoparticles (NPs) as heterogeneous catalysts are used in a wide range of applications such as organic synthesis [1], biorefinery [2], electrocatalysis [3,4], and environmental protection [5]. In particular, palladium (Pd) NPs have been widely investigated in cross-coupling [6], oxidation [7], decarbonylation [8], hydrogenation [9] and related reactions [10,11]. However, Pd NPs are generally unstable due to their large active surface areas and

suffer from self-aggregation problems, which impair their properties and limit their catalytic applications [12–14].

In order to solve the above problems, various strategies have been attempted to stabilize Pd NPs including confinement of them in solids, polymers or ligands [15–18]. For example, carbon materials, including graphene [19], carbon nanotubes [20] and carbon fibers [21], have been used to load Pd NPs, and these carbon-loaded Pd NPs exhibit high catalytic turnover frequency (TOF) values of $1068\text{--}2520 \text{ h}^{-1}$. Porous nanomaterials such as molecular sieves and metal-organic frameworks have also been used to anchor Pd NPs, and the Pd NPs confined within their nanopores exhibit excellent chemoselectivity of 99% at 353 K [22]. Recently, low-cost, nontoxic and biodegradable matters including chitosan, cellulose, and wood, have been used as natural templates for the syntheses of Pd NPs [23–26]. They are featured as having characteristics of renewability, sustainability, flexibility, hydrophilicity, biocompatibility, and easy processability. The combination of natural polymers and Pd NPs is highly expected to show unique advantages in catalytic reactions [27,28]. Nevertheless, the development of natural nanomaterials as novel subtle matrices for enhancing the catalytic activity and recyclability of Pd NPs is still in progress.

Nanocellulose has drawn broad attention due to its fine morphology, huge specific surface area, abundant active reaction groups, and decent stability both in water and most organic solvents [29]. The functionalized nanocellulose can be sustainable building blocks for constructing nanoscale matrices based on bottom-up assembly strategy to load Pd NPs [30]. For instance, cellulose nanocrystals (CNCs) were used as support materials of Pd NPs for catalytic hydrogenation at 293 K and

Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, China

[†] These authors contributed equally to this work.

^{*} Corresponding authors (emails: yuhapeng20000@nefu.edu.cn (Yu H); zhangxianquan2013@aliyun.com (Zhang X))

Heck coupling at 353–403 K [31–34]. In addition, 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO)-oxidized cellulose nanofibers (CNFs) were adopted as Pd carriers for using in discoloration of dyes and Suzuki reactions [35,36]. Although these attempts have made progress in the past, little attention has been laid on the spatial configuration of the as-prepared products, and the regulation of dense, even distribution of Pd NPs in CNF-assembled matrix and the resultant nano-confinement effect have barely caught attention. Thus, the catalytic route is usually rigid and restricted, and the room-temperature catalytic activity and chemoselectivity have not reached an ideal level.

In this study, a two-step synthesis method was proposed to fabricate high-loading and even-distributed Pd NPs with the CNF-assembled matrix as a chemical and spatial-confinement template (Scheme 1). A hydrated deep eutectic solvent (DES) combined with ultrasonic treatment was used to replace TEMPO to prepare carboxylic CNFs. The obtained carboxylic CNFs had high aspect ratios and rich carboxyl moieties, which provide a great possibility for them as carriers for *in situ* synthesis of Pd NPs. A three-dimensional (3D) hybrid foam of CNF with confined Pd NPs (CNF-Pd) was formed by simply freeze-drying the mixture of carboxylic CNFs and Pd NPs. The CNF-Pd hybrid foam was mainly composed of CNF-assembled mesoporous nanosheets, with even-distributed Pd NPs anchored on their surfaces. The nano-confinement effect, catalytic activity and recyclability of the CNF-Pd foam as a catalyst were investigated by the hydrogenation reaction of model compound 4-nitrophenol at room temperature. The chemoselectivity performance of the CNF-Pd catalyst was also studied in the hydrogenation of 3-nitrostyrene (NS) to 3-aminostyrene (AS) or 3-nitroethylbenzene (ENB).

EXPERIMENTAL SECTION

Preparation of carboxylic CNFs

Choline chloride and oxalic acid dihydrate were mixed

with a molar ratio of 1:1 at 80°C for 1 h to give a DES [37]. Cellulose pulp (0.5 g) was mixed with the DES (10 g) and water (10 g) in a Teflon-lined polyetheretherketone tank. The tank was heated at 110°C for 2 h to obtain carboxylic cellulose. The carboxylic cellulose was then diluted with water to a concentration of 0.4% w/v. The mixture was then treated using a JY99-IIDN ultrasonicator (20 kHz, Scientz Biotechnology Co., Ningbo, China) at 800 W for 15 min, resulting in 0.4% w/v carboxylic CNF suspension.

Synthesis of CNF-Pd

PdCl_2 (17.7 mg) was dissolved in HCl (1 mmol L⁻¹, 50 mL) at room temperature with a magnetic stirrer. The above solution (10 mL) was added into the CNF suspension (20 mL, 0.4 wt%) under vigorous stirring. An aqueous solution of NaBH_4 (10 mg, 1 mL) was added dropwise to the mixture which then reacted at 4°C for 4 h. The Cl^- and unbound Pd NPs were removed by dialysis with deionized (DI) water by using regenerated cellulose membranes (molecular weight cutoff: 12–14 kDa, Spectrum Laboratories Inc., Rancho Dominguez, CA, USA). After dialysis, the product was freeze-dried to CNF-Pd foam for use.

Characterizations

The carboxyl group ($-\text{COOH}$) content of CNFs was measured by conductometric titration with a DDS-11A conductivity meter (LEICI Instrument, Shanghai, China). Fourier transform infrared (FTIR) spectra were recorded over the absorbance range from 500 to 4000 cm⁻¹ by using a Nicolet Magna 560 FTIR instrument (Thermo Fisher Scientific Inc., Waltham, USA). The Pd content in the CNF-Pd was determined by inductively coupled plasma spectrometry (ICP, PE Optima8300, USA). The samples were digested using nitric acid/perchloric acid (5:1, v/v) with high-temperature sterilization at 200°C for 6 h. The resulting solutions were diluted to 10 ppb level for ICP analysis. X-ray photoelectron spectroscopy (XPS) analysis was performed by using a Ka system (Thermo

Scheme 1 Schematic illustration of a two-step confinement strategy for preparing the CNF-Pd catalyst.

Fisher Scientific, Basingstoke, West Sussex, UK) operated at 14 kV. Nitrogen sorption analysis was performed by using a 3H-2000PS2 Brunauer-Emmett-Teller (BET) surface area analyser (Beishide ST Ltd., Beijing, China). Specific surface area was calculated with the BET method. Pore volume and pore-size distribution were calculated by using the Barrett-Joyner-Halenda model based on the adsorption branches of the isotherms. X-ray diffraction (XRD) was performed on a D/max 2200 diffractometer (Rigaku, Japan), with Ni-filtered Cu K α radiation at 40 kV and 30 mA. The diffraction data were collected in the range of $2\theta = 10^\circ$ – 90° at a scanning rate of 2° min^{-1} . The Pd crystallite dimensions were calculated based on the Scherrer equation. A Tecnai G2 transmission electron microscope (TEM; FEI, USA) operated at 100 kV was used for TEM imaging. The CNFs were stained with phosphotungstic acid (1%) to enhance the contrast before TEM imaging. The samples were prepared by depositing 10 μL drop of 0.01% aqueous suspension on a carbon-coated TEM grid (300-mesh copper, formvar-carbon, Ted Pella Inc., USA). The sizes of Pd NPs were measured from the TEM images by using a TDY-V5.2 image analysis system (Tianhong Precision Instruments, Beijing, China). Scanning electron microscopy (SEM) images of samples were taken by using a JSM-7500F microscope (JEOL, Japan) at 15 kV. Before observation, the samples were coated with platinum by using a vacuum sputter coater. Elemental analysis and elemental mapping at the microstructural level were performed by the energy-dispersive X-ray spectrometry (EDS) attached to the SEM.

Catalytic performance of CNF-Pd

The room-temperature catalytic activity and recyclability of CNF-Pd were studied through catalytic hydrogenation of 4-nitrophenol to 4-aminophenol. Generally, 4-nitrophenol (0.5 mmol, 70 mg), CNF-Pd (5 mg, 9.6 wt% Pd loading) and NaBH_4 (2 mmol, 76 mg) were added in 10 mL of water with continuous stirring at room temperature. Ultraviolet-visible (UV-Vis) spectrophotometer (Lambda 750, Perkin Elmer, USA) was used to reflect the changes. After the indicated reaction time (typically 300–900 s), the CNF-Pd was recycled from the mixture by centrifugation and directly reused for a next catalytic reaction after washing properly with water. The products in aqueous solution were extracted with ethyl acetate (5 mL $\times$ 3), and the combined organic phase was concentrated *in vacuo* and filtered for analysis. The products were identified by gas chromatography-mass spectroscopy (GC-MS, Agilent 7890A-7000B, HP5-MS capillary column). The yield and selectivity were quantified by UV

and GC equipped with flame ionization detector (GC-FID, Agilent 7890B GC, HP5-MS capillary column). The temperature program consisted of $10^\circ\text{C min}^{-1}$ heating steps from 80 to 280°C .

The kinetic reaction rate constant (k) was calculated by Equation (1).

$$\ln(C_t / C_0) = -kt, \quad (1)$$

where C_0 and C_t correspond to the concentrations of nitrophenol at initial time and reaction time t .

The TOF value was calculated based on Equation (2).

$$\text{TOF} = \frac{\text{mole of converted substrate}}{\text{mole catalyst} \times \text{reaction time}}. \quad (2)$$

Catalytic hydrogenation of NS was used to verify the chemoselectivity of CNF-Pd combined with different solvents. Generally, NS (0.5 mmol, 75 mg), CNF-Pd (5 mg, 9.6 wt% Pd loading) and NaBH_4 (2 mmol, 76 mg) were added in 10 mL of water or alcohol/water co-solvent with continuous stirring at room temperature. After the indicated reaction time (typically 1–3 h), the products were separated from CNF-Pd by centrifugation and concentrated *in vacuo*. Ethyl acetate (5 mL $\times$ 3) was used for extraction and the combined organic phase was concentrated *in vacuo* and filtered for analysis. The products were identified and quantified by GC-MS and GC-FID as previously described.

RESULTS AND DISCUSSION

The carboxyl content of CNFs should first be concerned because they are responsible for the confinement of dense and uniform Pd NPs on their surfaces. More carboxyl groups on CNFs can provide more active sites for anchoring Pd^{2+} ions. The DES pretreatment is considered as an environmentally friendly method for both the preparation and the carboxylation of CNFs [37–40]. Here, a 50% hydrated choline chloride/oxalic acid dihydrate DES was used to pretreat the cellulose to produce carboxylic CNFs. As listed in Table 1, the carboxyl content increased with the reaction time, but the yield of CNFs decreased in the meantime. Therefore, a reaction time of 4 h seemed too long for the pretreatment, because the CNF yield dropped significantly to 58% due to severe degradation during the process. Considering both the yield and the carboxyl content, a reaction time of 2 h was deemed optimal. The hydrated DES pretreatment also promoted the ultrasonic nanofibrillation of CNFs, and homogeneous CNF suspension was obtained as shown in Fig. S1. The diameters of CNFs mainly concentrated in 5–10 nm, and the aspect ratios were as high as several hundred (Fig. S2). The presence of FTIR absorption peak at 1725 cm^{-1} in-

Table 1 Yields and carboxyl contents of CNFs after various reaction times in hydrated DES

Sample	Reaction time (h)	Yield (wt%)	-COOH (mmol g ⁻¹)
CNFs	0.5	99.98	0.068
	1.0	87.51	0.113
	2.0	80.62	0.164
	4.0	58.00	0.213

indicated the existence of C=O due to the DES pretreatment (Fig. S3). Other absorption peaks at 1637, 1424, 1373, 1108, 1027 and 890 cm⁻¹ agreed well with those of pure cellulose.

The CNF-Pd was synthesized through a two-step confinement process (Scheme 1). During the process, UV-Vis spectra were recorded to reflect the chemical crosslinking reactions (Fig. 1a). The PdCl₂ solution originally showed typical absorption peaks of Pd²⁺ at 208 and 233 nm. When Pd²⁺ was chemically crosslinked with the carboxyl groups of CNFs, their homogeneous CNF-Pd suspension still showed typical absorption peaks as those of PdCl₂ solution. After the *in situ* reduction by adding NaBH₄, the color of the mixture solution changed from light yellow to

black (Fig. 1a inset), and typical Pd²⁺ absorption peaks disappeared from the UV-Vis spectrum. This was consistent with the reduction of Pd(II) to Pd(0) [41]. The CNF-Pd suspension was stable even after a deposition of six months (Fig. S4a).

When the CNF-Pd suspension was freeze-dried into CNF-Pd foam (Fig. S4b), its phase structure was detected by XRD (Fig. 1b). The diffraction peaks at 2θ = 40.0°, 46.4°, 68.0°, and 82.0° in the curve of CNF-Pd corresponded to the (111), (200), (220), and (311) lattice planes of Pd (JCPDS# 46-1043). Typical cellulose I peaks corresponding to the (110) and (200) lattice planes were also observed, suggesting the hydrated DES pretreatment and NaBH₄ reduction process did not change the crystal type of cellulose.

The chemical bonding state between CNF and Pd was further investigated by XPS. The peaks of C, O and Pd elements were found in the wide-scan spectra of CNF-Pd (Fig. 1c). From the high-resolution scan spectrum of Pd 3d (Fig. 1d), the Pd⁰ 3d_{5/2} and 3d_{3/2} peaks at 334.9 and 340.6 eV could be identified clearly. Pd in the oxidation state (peaks at 336.8 eV) was also found, which was possibly due to the coordination of Pd NPs with carboxyl/

Figure 1 Physicochemical characterizations of the as-prepared CNF-Pd. (a) UV-Vis spectra and photos (inset) of PdCl₂, 0.4 wt% CNF suspension, mixture solution of 0.4 wt% CNF and PdCl₂, and the resulting CNF-Pd suspension after adding NaBH₄; (b) XRD spectra of CNF-Pd, CNF and Pd (JCPDS# 46-1043); (c) XPS spectra of CNF-Pd and CNF; (d) the high-resolution scan spectra of Pd 3d.

hydroxyl groups of CNFs or oxidation in the air [42–44]. The peaks of C 1s at 284.8, 286.3 and 287.3 eV indicated the co-existence of C–C, C–O, O–C–O bonds and the peaks of O 1s at 533.1 and 532.4 eV also confirmed the existence of C–O–C and C–OH bonds (Fig. S5). The binding energy of C=O bond showed an increase from 288.1 to 288.7 eV in C 1s and a reduction from 531.7 to 531.5 eV in O 1s, which implied C=O as the main coordination binding mode with Pd NPs. These results revealed that metal Pd had been chemically confined in the CNF-Pd.

The morphology and size distribution of Pd NPs confined in CNF-Pd were further observed by TEM and SEM. The TEM image in Fig. 2a shows even-dispersed torispherical Pd NPs on the CNF substrate. Because the observation of Pd NPs did not need a phosphotungstic acid staining treatment, the non-conducting CNFs were hardly to distinguish. The sizes of Pd NPs measured from a high resolution TEM (HRTEM) image (Fig. 2b) ranged from 3 to 8 nm, and the average diameter was 6.2 nm (Fig. 2d), close to that calculated from XRD by using the Scherrer equation (6.4 nm). The lattice fringe spacing was measured as 0.23 nm from Fig. 2c, also consistent with the Pd(111) lattice spacing of face centered cubic struc-

ture [45].

The microstructure of CNF-Pd was 3D cellular-like at low magnification (Fig. 3a). With the magnification increase, it was found that the CNF-Pd foam consisted of CNF-based nanosheets, which were constituted by the interlaced CNFs (Fig. 3b and inset). Massive mesopores were formed within the CNFs and evenly distributed throughout the nanosheets (Fig. 3c). The EDS mapping of C, O, and Pd elements proved that Pd NPs were also evenly distributed across the whole nanosheets (Fig. 3d–f and Fig. S6). The ICP analysis gave a high Pd content of 9.6 wt% for the CNF-Pd. The specific surface area of the CNF-Pd was $20.9 \text{ m}^2 \text{ g}^{-1}$ by the BET method, with a peak pore diameter of 5 nm (Fig. S7). Such a porous nanostructure was conducive to improving the fluid accessibility and providing sufficient active sites, and it therefore can enhance the reaction efficiency within the nano-domains [27,46].

Catalytic hydrogenation of 4-nitrophenol was used as a model reaction to evaluate the catalytic activity of CNF-Pd. As shown in Fig. 4a, the absorption peak at 400 nm belongs to 4-nitrophenolate ion with the addition of NaBH_4 in aqueous solution. Fig. 4b shows the UV-Vis absorption spectra of the reaction mixtures correspond-

Figure 2 Morphology of the synthesized Pd NPs on CNFs: (a–c) TEM images and (d) size distribution of the Pd NPs.

Figure 3 (a) SEM images of the CNF-Pd at (a, b) low magnification and (c) high magnification. The insets are diagrams of the CNF-Pd at different scales. (d–f) EDS mapping images of C, O and Pd elements.

Figure 4 Use of CNF-Pd in the hydrogenation of 4-nitrophenol to 4-aminophenol at room temperature: (a) UV-Vis absorption spectra of 4-nitrophenolate ions with (red curve) or without (black curve) NaBH_4 in the aqueous solution; (b) UV-Vis absorption spectra of the reagents at different reaction times (insets show the photos of the color change before and after the reaction with the corresponding molecular structures); (c) $\ln(C_t/C_0)$ versus reaction time of CNF-Pd and Pd NPs (without CNF confinement) as a catalyst, respectively; (d) recycle uses of CNF-Pd for six successive cycles.

ing to different reaction times. The absorption peak at 400 nm gradually decreased with the reaction time. A new peak at 300 nm corresponding to 4-aminophenol

emerged and its intensity also increased with the reaction time. The k of CNF-Pd was $8.8 \times 10^{-3} \text{ s}^{-1}$, apparently higher than $2.82 \times 10^{-3} \text{ s}^{-1}$ of the Pd NPs without CNF

Table 2 The catalytic activity of CNF-Pd compared with other matrix-supported Pd catalysts in literatures for the catalytic reduction of 4-nitrophenol

Entry	Sample	Pd loading (wt%)	k ($\times 10^{-3} \text{ s}^{-1}$)	TOF (h^{-1})	Ref.
1	CNF-Pd	9.6	8.8	2640	This work
2	Pd NPs	—	2.8	436	Control
3	Pd/chitosan	15	4.1	—	[27]
4	Pd@PANI-CS- Fe_3O_4	3.5	3.7	1994	[48]
5	Pd-NiO	4.85	4.8	—	[49]
6	Pd/ CeO_2	0.2	8.0	1068	[50]
7	Pd/GO	7.5	4.5	—	[51]
8	Pd-CNT	9.8	6.2	810	[52]
9	Pd-C/N	0.52	7.0	2520	[53]
10	Pd@MIL	1.57	6.5	2088	[54]
11	Pd@VP2	7.7	3.7	1980	[55]

confinement (Fig. 4c). The TOF value of CNF-Pd was 2640 h^{-1} , six times higher than that of Pd NPs without CNF confinement (436 h^{-1}) (Table S1). When comparing the TOF and k values of CNF-Pd with other matrix-supported Pd catalysts (Table 2), the CNF-Pd showed higher catalytic efficiency than most of Pd catalysts with chitosan and carbon substrates, and comparable catalytic efficiency to those of Pd catalysts supported on metal oxide substrates. Such superior catalytic activity of CNF-Pd could be ascribed to its abundant nanopores within the 3D structure and dense spatial confinement of Pd NPs on hydrophilic substrates. Therefore, the CNF-Pd could be reused at least six successive cycles without losing activity (Fig. 4d), showing good recyclability.

A possible explanation for the high catalytic performance of CNF-Pd was proposed. The catalytic mechanism of the hydrogenation of 4-nitrophenol involves the electron transfer from the BH_4^- donor to the 4-nitrophenol acceptor following the Langmuir-Hinshel-Wood mechanism [47]. NaBH_4 has a high theoretical hydrogen capacity, and H_2 can be released under alcohol/water condition. The CNF-Pd has a 3D nanoporous structure with abundant active catalytic sites which can generate spatial nano-confinement effect on the 4-nitrophenol. In the nanopores of CNF-Pd, the increased effective concentration of 4-nitrophenolate ions and more H-Pd bonds were formed by attaching to CNF-Pd surfaces, enhancing the catalytic activity. After the electron transfer finished, H^+ and 4-aminophenolate ions rearranged and 4-aminophenol desorbed from the CNF-Pd surfaces. These results suggest that the confinement of Pd within CNF matrices not only enhanced the catalytic activity but also improved the catalyst stability.

NS was used as a model compound to investigate the

chemoselective activity of the CNF-Pd. Scheme 2 shows two possible hydrogenation reaction routes of NS [56]. One route is selective hydrogenation of the nitro group in NS to give AS; the other is selective hydrogenation of double bond in NS to generate ENB. Regardless of which route is initially followed, excessive hydrogenation of the products eventually produces 3-ethylaniline (EA).

Both solvent and reaction time were investigated for chemoselective conversion of NS with NaBH_4 and CNF-Pd. It was found that the catalytic activity order of the solvent is methyl alcohol (MeOH) > water > ethanol (EtOH) > ethylene glycol (MEG) (Table 3). The use of MEG or EtOH as solvent with a reaction time of 3 h could produce ENB with excellent selectivity of 100%, but the conversion was relatively low (Table 3, entries 1, 2). The final hydrogenation product EA was obtained with MeOH or water as solvent and a reaction time of 3 h, and the conversion reached 100% (entries 3, 4). These results indicate that the solvent played an important role in the selectivity of catalytic route [57]. Chemoselective conversion of NS to AS could be obtained with 80%–98% yield by choosing water, MeOH , or water/ MeOH (1:1,

Scheme 2 Chemoselective conversion of NS to AS or ENB, and eventually EA.

Table 3 Chemoselective conversion of NS with NaBH₄ and CNF-Pd under different reaction conditions^a

No.	Catalyst	Solvent (10 mL)	Time (h)	Conversion of NS (%)	Selectivity (%)		
					AS	ENB	EA
1	CNF-Pd/NaBH ₄	MEG	3	13	0	100	0
2		EtOH	3	50	0	100	0
3		MeOH	3	100	0	0	100
4		Water	3	100	0	0	100
5		MeOH	1	100	96	0	4
6		Water	1	80	100	0	0
7		Water/MeOH ^b	1	98	100	0	0

a) Reaction conditions: NS (0.5 mmol), CNF-Pd (5 mg), NaBH₄ (2 mmol), room temperature; b) volume ratio of water and MeOH is 1:1.

v/v) as the solvent with a reaction time of 1 h (entries 5–7). Therefore, the combination of CNF-Pd and certain solvent can generate a chemoselectivity on the products. This is probably because protic solvents with higher hydrogen donating ability can help hydrogen transfer on the Pd NPs through the hydrogen spillover mechanism [58–60].

CONCLUSION

In summary, a highly active and recyclable CNF-Pd catalyst was fabricated by a facile and green route. Ultrafine Pd NPs with an average diameter of 6.2 nm were spatially confined in the CNF matrices, with a high loading of 9.6 wt%. The CNF-Pd showed high room-temperature catalytic activity in the hydrogenation of 4-nitrophenol by NaBH₄. The reaction rate constant was $8.8 \times 10^{-3} \text{ s}^{-1}$, and the TOF value reached 2640 h^{-1} , which were far higher than those of Pd NPs without CNF confinement. The CNF-Pd was reusable even after six successive cycles due to the chemical immobilization of Pd NPs. The combination of CNF-Pd and suitable solvent could exhibit good chemoselectivity in the conversion of NS. Overall, we demonstrate a facile strategy to prepare recyclable Pd NPs by CNF confinement with enhanced catalytic activity and chemoselectivity.

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Supplementary information Supporting data are available in the online version of the paper.

Juan Meng is currently a PhD candidate at Northeast Forestry University, China. She received her BSc degree in wood science and engineering from Anhui Agricultural University in 2016. Her research interest focuses on the design and synthesis of biomass-based nanomaterials for catalytic applications.

Yongzhuang Liu received his PhD degree in 2019 from Northeast Forestry University, China. He was a visiting student at the University of Groningen, the Netherlands during 2018–2019. Now he is an associate professor at the Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University. His research interest lies in the valorization of lignocellulosic renewable materials using green solvents.

Haipeng Yu received his PhD degree in 2005 from Northeast Forestry University, China. He is currently a full professor at the Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University. His research interest focuses on the green conversion of sustainable biomass for developing bio-based functional materials. Currently, he is interested in the cellulose and nanocellulose-based functional materials, including catalytic materials, energy storage materials and flexible intelligent electronics.

纳米纤维素限域钯纳米颗粒的室温催化活性及化学选择性

孟娟[†], 刘永壮[†], 史晓超, 陈文帅, 张显权*, 于海鹏*

摘要 本文利用水合低共熔溶剂结合超声法制备了羧基化纤维素纳米纤丝(CNF), 并利用其表面的羧基官能团为反应活性位点原位合成了具有均匀分散性和高负载量(9.6 wt%)的CNF-Pd复合催化剂. 研究表明: CNF-Pd具有显著的限域特性, 包括在CNF表面羧基官能团上原位固定生长Pd纳米颗粒的化学限域和CNF冷冻干燥过程中自组装形成的空间结构限域. CNF-Pd在4-硝基苯酚加氢模型反应中表现出优异的室温催化活性, 其最高速率常数为 $8.8 \times 10^{-3} \text{ s}^{-1}$, 最高催化活性的转化频率为 2640 h^{-1} . CNF-Pd催化剂在水性介质中显示出良好的化学稳定性和可回收性, 至少重复使用6个循环不会失活. 此外, CNF-Pd催化剂还可实现3-硝基苯乙烯在醇/水共溶剂中向3-氨基苯乙烯的化学选择性加氢, 且具有80%–98%的高选择性产率. 综合上述结果, CNF在构建具有高室温催化活性及可回收利用的金属纳米颗粒催化剂方面具有广泛应用潜力和发展空间.