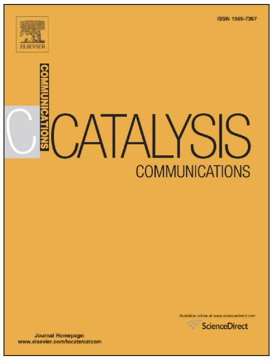

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Modified cellulose with tunable surface hydrophilicity/hydrophobicity as a novel catalyst support for selective reduction of nitrobenzene

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ABSTRACT

Cellulose with tailorable hydrophilicity/hydrophobicity were synthesized by grafting F-containing groups and utilized as supports for palladium nanoparticles. The obtained catalysts were applied in the synthesis of N-phenylhydroxylamine from controllable reduction of nitrobenzene. Unexpectedly high conversion and selectivity could be achieved with 25 ppm Pd catalyst at room temperature in water. The precise modification of the catalyst surface is crucial to realize this targeted transformation. Further investigation indicated that modified cellulose with a more hydrophobic surface would favour the adsorption of nitrobenzene over N-phenylhydroxylamine thus prevent full hydrogenation to aniline.

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1. Introduction

N-arylhydroxylamines represent an important class of chemical intermediates [1]. Selective reduction of nitroarenes is considered to be the most important and feasible strategy to produce N-arylhydroxylamines. At present, N-arylhydroxylamines are mainly produced by reduction of nitrobenzene with stoichiometric zinc as reductant [2, 3], which is an environmentally unfriendly strategy. Compared with the traditional reduction procedure, metal-catalytic reduction is regarded as a greener methodology to produce N-arylhydroxylamines. However, catalytic reduction of nitroarenes is a consecutive process, and usually continues until anilines were formed [4-6]. Therefore, improving the selectivity of N-arylhydroxylamines has long been a significant challenge. Recently, several rhodium and platinum catalysts have been reported to be efficient catalysts for selective reduction of nitrobenzene[7-11]. However, few reports about Pd-catalyzed selective reduction of nitroarenes to N-arylhydroxylamines was reported [12], because the high activity of Pd catalysts might lead to over-reduction[13-15]. Inspired by previous works, we turned to study approaches to enhance the selectivity of Pd catalysts.

Recently, tuning the catalytic activity and selectivity by surface modification has generated a tremendous level of attention [16-18]. Most surface modification, especially hydrophilicity/hydrophobicity regulation, can strongly affect the adsorption/desorption of reactants and the reaction intermediates on the catalyst surface and thus improve the activity and/or selectivity of the product[19, 20]. For example, a hydrophobic surface can enrich a hydrophobic reactant around active sites in aqueous phase and then accelerate the corresponding reactions[21, 22]. In the case of synthesis of N-phenylhydroxylamine (PHA), hydrophobic surface of catalysts will enrich hydrophobic nitrobenzene and repel the adsorption of hydrophilic PHA, and thus prevent further reduction of PHA. In this study, naturally renewable cellulose was chosen as the catalyst support for the presence of a large number of modifiable hydroxyl groups[23-25]. Cellulose is a super-hydrophilic polymer that can be evenly dispersed in water. On the other hand, fluorine possess unique properties, such as high electronegativity and relatively small size. Thus fluorine usually has unexpected influence on the properties of a given compound or support [26-28]. Furthermore, the F-containing groups modified surface was reported to be highly hydrophobic[29], which was supposed to make the modified materials more suitable for organic reactions in aqueous media. Modification of cellulose by attaching highly hydrophobic F-containing groups would be a great choice for surface hydrophilicity/hydrophobicity regulation of cellulose.

Herein, we reported the synthesis of perfluoroalkyl-modified cellulose supported ultra-small Pd NPs *via* a solid state method. The obtained Pd catalyst exhibited excellent activity and selectivity in the reduction of nitrobenzene to PHA under mild conditions. The Pd catalyst amount used in this reaction is as low as 25 ppm. The small size of Pd NPs and the influence of F-containing groups were supposed to be the main reasons for the high activity and selectivity of Pd catalysts.

2. Experimental Section

2.1. Cellulose modification

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In a typical procedure, α-cellulose (1 g) was dispersed in dry DMF (10 mL). Then the mixture was sonicated for 30 min to obtain equally distributed cellulose suspension. The suspension was cooled to 0 °C and NaH (700 mg) was added in two portions. After stirring for 30 min, 1H, 1H, 2H, 2H-perfluoroalkyl iodide (1g) was slowly added and the reaction mixture was warmed to room temperature. After stirring overnight, the reaction mixture was filtrated. The solid was washed with DMF, deionized water and ethanol before dried at 60 °C for 10 h. The final product was obtained as yellowish solid and denoted as C_nF_{2n+1}-Cell.

2.2. Catalysts preparation.

A 300 mg amount of C_nF_{2n+1}-Cell and 10 µL 5 mg/mL $PdCl_2$ solution was mixed and milled manually for 20 min in an agate mortar. The samples were kept for 24 h to achieve adsorption of Pd ions on the surface of Cellulose. Thereafter, 60 mg of sodium formate was added to the powder mixture and ground for 30 min and kept for another 24 h. The as-prepared samples were washed repeatedly with distilled water and ethanol to remove unreacted $PdCl_2$ and sodium formate. The obtained samples (Pd@ C_nF_{2n+1}-Cell) were dried in in vacuum oven at 25 °C for 12 h.

2.3. Hydrogenation of nitrobenzene.

Typically, 0.2 mmol nitrobenzene, sodium borohydride, catalyst and 3mL distilled water was added into a 15mL tube, then the tube was sealed with a polytetrafluoroethylene plug. The mixture was stirred at 30°C and monitored by TLC. Upon completion of the reaction, catalysts were separated by centrifugation. The reaction mixture was analyzed by HPLC.

2.4. Adsorption experiments.

The adsorption experiments were carried out at room temperature. Catalysts (3mg) was dispersed in 1 mL water solutions containing various concentrations of nitrobenzene or PHA. After vigorous stir for 10 min, the catalyst were separated by centrifugation. The remained amounts of nitrobenzene or PHA in the supernatants were analyzed by HPLC. The amounts of nitrobenzene or PHA adsorbed on the surface of catalysts were determined by the change of concentrations before and after adsorption. For the HPLC measurement, 1-hexanol was introduced as an internal standard in the methanol solution,

2.5. Characterization.

TEM images were taken using a PHILIPS Tecnai 12 microscope operating at 120kv. Energy Dispersive X-ray Spectroscopic analysis (EDS) was performed with a JEM-2010(HR) transmission electron microscope at an acceleration voltage of 200kV. High Resolution Transmission electron microscopy (HRTEM) was performed on Philips-FEI Tecnai G2 F20 operating at 300kv. X-ray photoelectron spectroscopy (XPS) were performed on a ESCALAB 250Xi spectrometer, using a Al Kα X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.60 eV. Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV.

3. Results and discussion

3.1. Characterization of Pd/Cell and Pd/C_6F_{13}-Cell

The morphologies and microstructures of the obtained catalysts were characterized by SEM and TEM. The SEM images of Pd/Cell and Pd/C_6F_{13}-Cell in Fig. S1 indicate that C_6F_{13}-Cell has a much rougher surface compared with pristine cellulose, which can benefit the adsorption of Pd ions onto support surface. Pd NPs were unable to see because of their tiny size and low loading on both Cell and C_6F_{13}-Cell. Distribution of Pd NPs on C_6F_{13}-Cell surface was investigated by TEM (Fig. 1a and S2). Fig. 1a revealed that Pd NPs in round shape are uniformly dispersed on C_6F_{13}-Cell and size of the NPs mainly distribute among 1.0 and 2.5nm. The uniform dispersion of Pd NPs was also exhibited in HAADF-STEM images (Fig. S3). It was apparent that Pd NPs in Pd/C_6F_{13}-Cell are much smaller compared to Pd NPs supported on pristine cellulose (Fig. S4). The comparison suggests that fluorinated compounds may benefit the stabilization of Pd[30, 31], resulting in smaller NPs. The ultrafine NPs can provide more contact opportunities between the reactants and the active sites, which was the prerequisite for high catalytic activity. Moreover, the image showed no aggregation of Pd NPs to a large degree (Fig. S2). HRTEM analysis was carried out to verify the formation of Pd NPs (Fig. 1b), as shown in Fig. 1b, the NPs have clear crystalline fringe patterns and the lattice distance is measured to be 0.23nm, which coulpd be assigned to the d-spacing of the (111) plane of Pd^0. Furthermore, the element mappings (Fig. S5) reveals that F and Pd atoms are uniformly distributed on the surface of cellulose. Therefore, we can confirm that the cellulose supported small Pd NPs catalyst with F-containing groups modified the cellulose surface, was successfully prepared *via* the solid-state pathway.

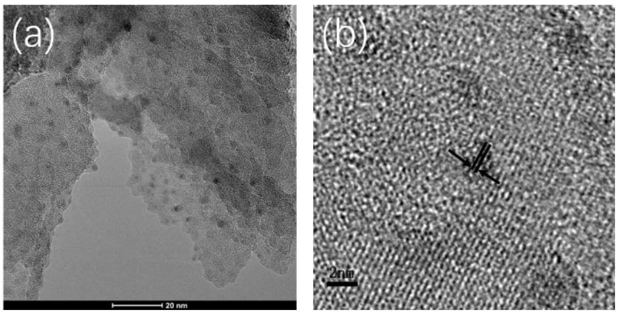


Fig. 1 (a) TEM and (b) HRTEM images of Pd/C_6F_{13}-Cell.

Since the modification of cellulose was confirmed to be successful, the effect of F-containing groups on the hydrophilicity/hydrophobicity was further investigated. The air–water contact angles on the surface of Cell and C_6F_{13}-Cell are 18.05° and 42.68° (Fig.S6a and S6c). In order to regulate the hydrophilicity/hydrophobicity of cellulose surface, cellulose with different surface modifiers were also synthesized. As displayed in Fig.S6 perflourine-alkyl with a shorter length led to a lower air–water contact angle, 30.89 ^{o}, while longer perflourine-alkyl led to a higher air–water contact angle, 65.70^{o} (Fig.S6b and S6d). Although grafting F-containing modifiers makes cellulose surface more hydrophobic, modified cellulose still retained great hydrophilic nature, which make them prefect supports for reactions in aqueous phase.

XPS measurements were carried out to further investigate the chemical state of surface atoms in Pd/C_6F_{13}-Cell (Fig. 2, S7, S8 and S9) and Pd/Cell (Fig. 2, S10 and S11). In Fig. S7, the survey clearly exhibits the presence of C, O, F and Pd elements in Pd/C_6F_{13}-Cell surface. However, due to the low content of Pd of 0.01% (Table S2), XPS peaks of Pd 3d could not be identified. So the XPS characterization of Pd was carried out with 0.5% Pd/C_6F_{13}-Cell. The Pd 3d region spectrum reveals that Pd^0 and Pd^{2+} coexist on the surface of the catalyst. According to the calculation from the XPS Pd 3d peaks, the Pd element mainly exists in metallic state (Table S1). A small amount of Pd was oxidized under ambient conditions, resulting in Pd^{2+} species. There is an obvious shift of binding energy of Pd^0 $3d_{5/2}$ compared with Pd^0 supported on cellulose without F-containing modifiers, indicating the electron transfer between F and Pd NPs. The distribution of Pd species calculated from the XPS Pd 3d peaks, shows that the contents of the Pd^0 in Pd/C_6F_{13}-Cell and Pd/Cell were 79% and 58%, respectively (Table S1), the slight difference might because of the storage environment and characterization process.

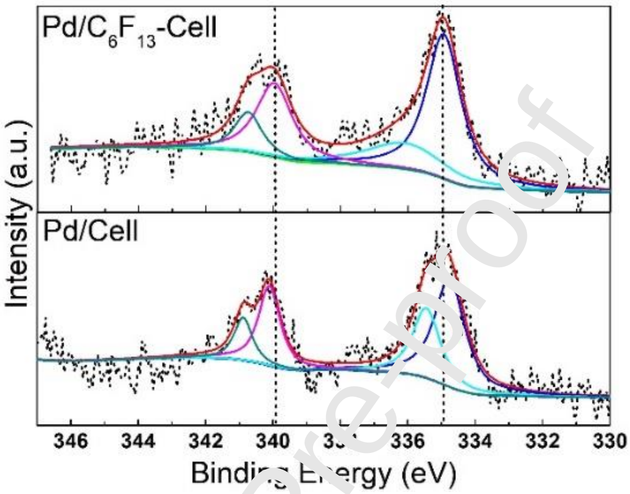


Fig. 2 Pd 3d XPS spectrum of Pd/C_6F_{13}-Cell and Pd/Cell.

3.2. Catalytic performance of the catalysts

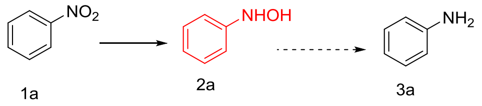
In the selective reduction of nitrobenzene to PHA, water was chosen as a green solvent considering its environmentally friendly nature. The catalytic performances of the catalysts with different perfluoroalkyl groups were displayed in Table 1, entries 1-5. Pd/Cell gave lowest nitrobenzene conversion and moderate selectivity to PHA (entry 1). As for the F-containing catalysts, the results clearly demonstrate that longer perfluoro-carbon chain gave higher catalytic activity. Pd/C_8F_{17}-Cell showed highest activity with almost 100% conversion of nitrobenzene but only 83% PHA in 1 h (entry 4), which might because the higher activity resulted in accumulation of nitrosobenzene intermediate , then nitrosobenzene and in situ converted PHA readily condenses to azoxybenzene[32]. Shorter time resulted in higher selectivity but lower conversion of nitrobenzene (entry 5). Pd/C_4F_9-Cell gave only 70% conversion of nitrobenzene while Pd/C_6F_{13}-Cell gave almost full conversion and 95% selectivity to PHA (entries 2 and 3). It is obvious that Pd/C_6F_{13}-Cell has the best performance in the reduction of nitrobenzene with excellent conversion and selectivity. Moreover, the results clearly indicate that modification of Pd/Cell with perfluoroalkyl groups can not only improve the activity but also the selectivity of the catalyst.

With the most suitable catalyst in hand, the reaction conditions was optimized. First, the effect of catalyst amount was examined. Excellent conversion and selectivity can be achieved with 25 ppm Pd/C_6F_{13}-Cell (entry 6). Little over-reduction occurred over 75 ppm catalyst, (entry 7). However, when the reaction temperature was increased to 50 ^{o}C, aniline was determined to be the main product with a selectivity of 64% and 12% azoxybenzene was also detected (entry 8), which is expected because higher temperature usually cause over-reduction of nitrobenzene. At last, the amount of reducing agent was optimized. Nitrobenzene can only be partly converted with 2.0 equivalent or 1.0 equivalent $NaBH_4$ (entries 9-10) and can hardly be reduced with 0.5 equivalent $NaBH_4$ (entry 11) at 30 ^{o}C. Therefore, the optimized reaction conditions for selective reduction of nitrobenzene to PHA was 30 ^{o}C with 3.0 equivalent $NaBH_4$ over 25 ppm Pd/C_6F_{13}-Cell.

The process of reduction reaction catalysed by Pd/C_6F_{13}-Cell was further studied by tracing the concentrations of reactant and products along with the reaction time (Fig. 3). The initial reaction rate was fast in terms of nitrobenzene conversion and formation of PHA. In the first hour, little aniline and azoxybenzene was detected. After complete consumption of nitrobenzene, PHA, formed up to 95%, was obtained as the main product of the first period. In the second period, azoxybenzene and aniline were formed in a relatively slow rate along with the consumption of PHA. After another 2h, aniline was the main final product.

Table 1

Evaluation of the reaction parameters on the selective reducion of nitrobenzene to PHA ^{a}.



Entry	Cat. (ppm)	[H]		Con.(%) [b]	Sel.(%)[b]
1	Pd/Cell(50)	$NaBH_4$(3.0)	30	43	75
2	Pd/C_4F_9-Cell(50)	$NaBH_4$(3.0)	30	70	92
3	Pd/C_6F_{13}-Cell(50)	$NaBH_4$(3.0)	30	98	95(89[c])
4	Pd/C_8F_{17}-Cell(50)	$NaBH_4$(3.0)	30	>99	83
5[d]	Pd/C_8F_{17}-Cell(50)	$NaBH_4$(3.0)	30	86	91
6	Pd/C_6F_{13}-Cell(25)	$NaBH_4$(3.0)	30	98	96
7	Pd/C_6F_{13}-Cell(75)	$NaBH_4$(3.0)	30	>99	93
8	Pd/C_6F_{13}-Cell(50)	$NaBH_4$(3.0)	50	>99	24
9	Pd/C_6F_{13}-Cell(50)	$NaBH_4$(2.0)	30	49	>99
10	Pd/C_6F_{13}-Cell(50)	$NaBH_4$(1.0)	30	13	>99
11	Pd/C_6F_{13}-Cell(50)	$NaBH_4$(0.5)	30	<1	-

[a] Reaction condition: the reaction was carried out under air atmosphere in 3 mL water containing 0.2 mmol of nitrobene. Catalyst amount based on Pd. [b] Determined by HPL**C.** [c] Isolated yield. **[d]** Reaction time was 30min.

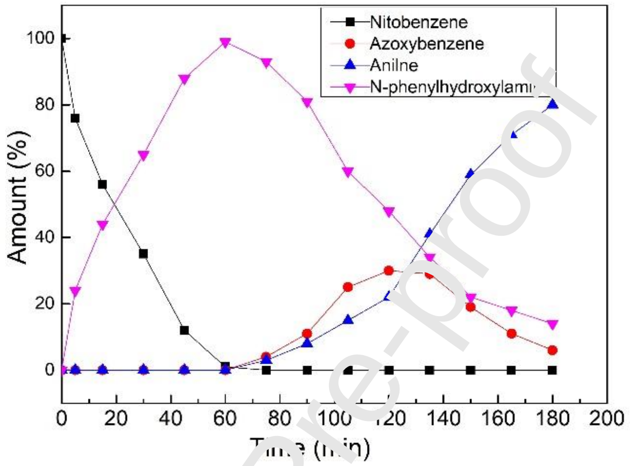


Fig. 3 Reaction profile for nitrobenzene reduction. Reaction condition: the reaction was carried out in 3 mL water containing 0.2 mmol of nitrobenzene at 30 °C. Pd amount is 25ppm.

In order to investigate the role of surface property in the high activity and selectivity, adsorption behaviour of nitrobenzene and PHA on Pd/Cell and Pd/C_6F_{13}-Cell was studied (Fig. 4). The adsorption curve of nitrobenzene apparently shows more nitrobenzene was adsorbed by Pd/C_6F_{13}-Cell (508 μmol/g catalyst) at the same nitrobenzene concentration compared with nitrobenzene was adsorbed by Pd/ Cell (315 μmol/g catalyst). The adsorption capacity of Pd/C_6F_{13}-Cell for PHA was 53 μmol/g catalyst, which was much lower than the adsorption capacity of Pd/Cell of 226 μmol/g catalyst. The enrichment of reactants around the catalyst will accelerate the reduction reaction. After PHA was formed, PHA could rapidly desorb form Pd/C_6F_{13}-Cell catalyst. This explains the slow rate of the conversion of PHA to aniline and azoxybenzene over Pd/C_6F_{13}-Cell. It can be inferred that modified cellulose could accelerate the conversion of nitrobenzene but prevent the further reduction of PHA. Therefore, the surface property played a critical role in the selective reduction of nitrobenzene and was the decisive factor that affect the final product.

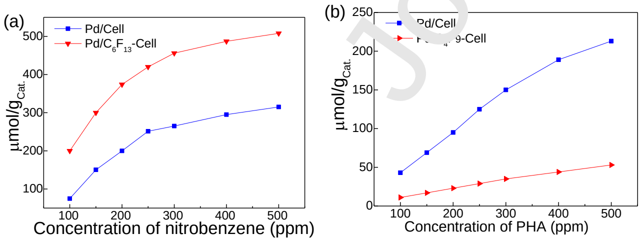


Fig. 4 Adsorption of (a) nitrobenzene and (b) PHA on Pd/Cell and Pd/C_6F_{17}-Cell

3.3. Recyclability of Pd/C_6F_{13}-Cell

Finally, reusability of the Pd/C_6F_{13}-Cell catalyst was also investigated. Catalysts were separated by centrifugation, washed with deionized water and directly used in next cycle without further drying. As shown in Fig. S14, the catalyst delivered excellent catalytic activity and selectivity for at least five cycles. After 5 runs, the conversion was decreased to 80% while the selectivity remained up to 96%, indicating the activity of the Pd/C_6F_{13}-Cell catalyst decreased with the reuse number but the selectivity was not affected by the recycle procedure. ICP characterization of recycled Pd/C_6F_{13}-Cell catalyst shows slight leaching of Pd (Table S2). Increase in the size of Pd NPs and slight agglomeration were observed in the TEM images of the recycled catalyst (Figure S15). Moreover, the reused catalyst was characterized by XPS, oxidation of Pd was also observed(Figure S17 and Table S1). The characterization and the recycling results indicated that the Pd content and particle size and valence state of Pd has no influence on the catalyst selectivity.

4. Conclusions

In summary, perfluorohexyl modified cellulose was successfully synthesized and utilized as support for Pd NPs. The obtained catalyst showed unexpected high activity and selectivity to the selective reduction of nitrobenzene to PHA. The excellent catalytic performance of Pd/C_6F_{13}-Cell is mainly attributed to the following reasons:

(i) F-containing modifiers would alter the adsorption behaviour of N-containing aromatics on catalysts. Modified cellulose has strong absorbability for nitrobenzene but weak absorbability for PHA, which could improve not only the activity but also the selectivity.

(ii) The ultrafine size of Pd NPs ensures well contact between the active sites and the reactants.

(iii) Presence of F-containing groups results in the enrichment of electrons on the metal surfaces for Pd/C_6F_{13}-Cell and lead to higher Pd^0 content

The outstanding catalytic performance Pd/C_6F_{13}-Cell in our work indicates regulated hydrophilicity/hydrophobicity play an important role in selectivity reduction, and we believe that the superior modified cellulose may have promising potential for the organic synthesis.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Credit Author Statement

Author contributions

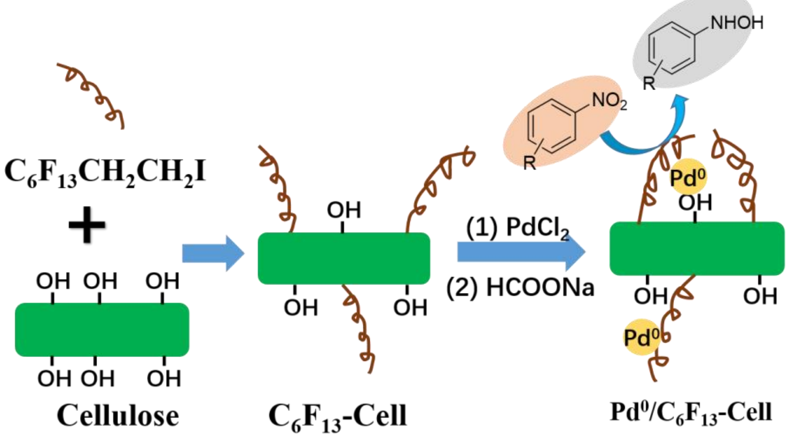
Dan-dan Li: Conceptualization, Methodology, Software, Investigation, Formal analysis, Data curation, Validation, Writing-Original Draft,:

Guo-ping Lu: Writing-Reviewing & Editing.

Chun Cai: Writing-Reviewing & Editing, Supervision

Declaration of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper


$C_6F_{13}CH_2CH_2I$
+
OH OH OH
OH OH OH
Cellulose
OH
OH
OH
C_6F_{13}-Cell
(1) $PdCl_2$
(2) HCOONa
NO_2
R
NHOH
R
Pd^0
OH
OH
OH
Pd^0
Pd^0/C_6F_{13}-Cell

Highlights:

- Cellulose with tunable surface hydrophilicity/hydrophobicity was synthesized.
- Pd nanoparticles on modified cellulose was prepared.
- Superior catalytic performance of reduction of nitrobenzene was achieved.
- Hydrophilicity/hydrophobicity of cellulose surface played a crucial role in the reaction.