


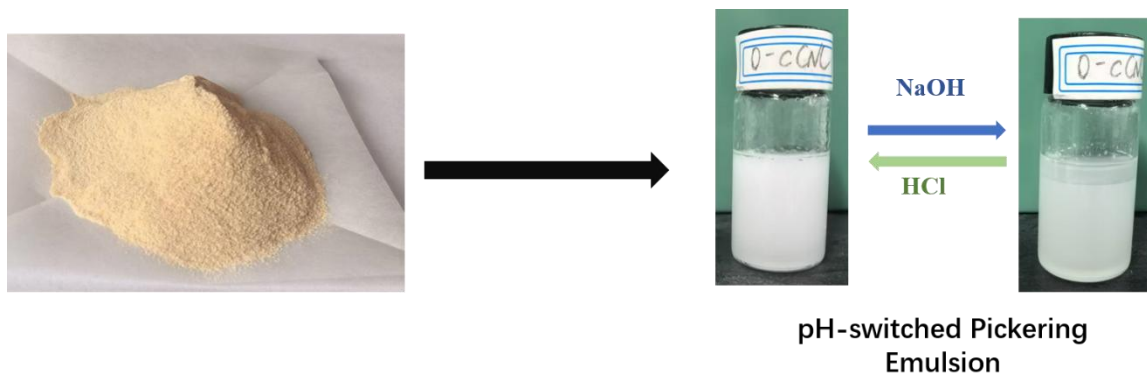
Pickering Emulsions Using Pd NP-loaded pH-sensitive Carboxylated Cellulose Nanocrystals for Catalytic Hydrogenation

Dandan Li ^a, Feichao Mia,^{a,b,*} Jinhua Chen,^b Zhibing Liu,^b Zhiyuan Wang,^a and Yang Wang^a


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GRAPHICAL ABSTRACT



Pickering Emulsions Using Pd NP-loaded pH-sensitive Carboxylated Cellulose Nanocrystals for Catalytic Hydrogenation

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Exploiting stimuli-responsive Pickering interfacial catalysts is crucial to the development of organic reactions in water and green chemistry. Herein, amphiphilic carboxylated cellulose nanocrystals were synthesized by surface modification of hydrophilic carboxylated cellulose nanocrystals. The obtained amphiphilic carboxylated cellulose nanocrystals showed great toluene-in-water Pickering emulsion stabilization capacity and pH-responsive property. Emulsification and rapid demulsification behaviours were observed by simple pH adjustment. Palladium nanoparticles supported on the amphiphilic carboxylated cellulose nanocrystals exhibited high activity in the hydrogenation reaction of nitrobenzene in aqueous media because of the improved mass transfer between hydrophobic substrate and hydrophilic solvent. Moreover, the pH-responsiveness of amphiphilic carboxylated cellulose nanocrystals could promote the recovery of both products and the Pickering interfacial catalyst. Therefore, palladium nanoparticles loaded bio-derived carboxylated cellulose nanocrystals for efficient pH-switched Pickering emulsion catalytic hydrogenation was successfully prepared. Outstanding activity and reusability were achieved.

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Keywords: Carboxylated cellulose nanocrystals; Pickering interfacial catalyst; pH-response; Hydrogenation

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INTRODUCTION

Pickering interfacial catalysts have attracted increasing attention due to environmental considerations and their high efficiency. Pickering emulsion offers significant advantages in catalytic reactions (Chang *et al.* 2021; Chen *et al.* 2023; Ma *et al.* 2024). They not only provide a large interfacial area but also reduce the diffusion distance of substrate molecules and minimizes mass transfer resistance (Dan *et al.* 2024). Due to the high stability of Pickering emulsions, a key challenge in Pickering interfacial catalysis is efficiently breaking the emulsion to separate products and catalysts after the reaction (Li *et al.* 2021). Mechanical methods, such as centrifugation to demulsify Pickering emulsions, can be complex and unsuitable for continuous large-scale production. Therefore, developing rapid, efficient, and sustainable methods for the recovery and reuse of Pickering interfacial catalysts is a critical aspect in advancing Pickering emulsion catalytic reaction systems. In this regard, stimuli-responsive Pickering emulsions are emerging as an ideal

class of catalytic systems due to their recyclability and facile separation. Pickering emulsifiers with surface-decorated stimuli-responsive moieties can respond to specific environmental factors, such as pH (Luo *et al.* 2020; Xiao *et al.* 2020; Zhang *et al.* 2024a), CO₂ (Li *et al.* 2024; Pei *et al.* 2024; Zhang *et al.* 2024b), temperature (Zhang *et al.* 2023), magnetism (Ma *et al.* 2021; Lu *et al.* 2022), and light (Richards and Evans 2022; Guo *et al.* 2024; Liu *et al.* 2024), allowing them to change their properties in response to these environmental stimuli. Thus, the recovery and reuse of Pickering emulsions could be conveniently handled.

Compared with synthetic polymers and modified inorganic materials, bio-based solid particles are renewable, result in less environmental pollution, and are widely sourced (Yokota *et al.* 2019; Meng *et al.* 2023; Qi *et al.* 2023). Recently, cellulose nanocrystals showed great Pickering emulsion stabilization capacity (Morais *et al.* 2023; Tiban Anrango *et al.* 2024; Zhang *et al.* 2024c). Cellulose nanocrystals (CNC)-based Pickering emulsion has been applied in wastewater treatment, food industry, and catalysis. However, lack of responses from external stimuli as the stabilizers of Pickering emulsions are the critical issues of CNC. In contrast, carboxylated cellulose nanocrystals (cCNC), usually obtained from oxidization of CNC (Guo *et al.* 2021; Gong *et al.* 2022; Wang *et al.* 2023), possess abundant carboxylic acid groups, which cause them to be pH-responsive (Wang *et al.* 2024; Wu *et al.* 2024). Therefore, cCNC seemed to be a promising stabilizer for stimuli-responsive Pickering emulsions. Nevertheless, cCNC are highly hydrophilic because of their numerous carboxylic acid and hydroxyl groups. For further utilization as Pickering emulsions stabilizer, the cCNC needs to be modified.

Herein, amphiphilic cCNC (O-cCNC) was prepared by grafting alkyl chains onto the surface of cCNC. After loading of Pd NPs, the obtained Pd/O-cCNC can stabilize toluene-in-water Pickering emulsion and promote aqueous hydrogenation of nitrobenzene. Benefiting from abundant carboxylic acid groups of cCNC, the rapid emulsification can be realized by simple pH regulation to recover products and catalysts rapidly.

EXPERIMENTAL

Materials

All chemical reagents were obtained from commercial suppliers and used without further purification. Carboxylated cellulose nanocrystals (cCNC) with an average length of 200 nm, n-octyltrimethoxysilane, palladium chloride (PdCl₂), sodium formate (HCOONa), and nitrobenzene were purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China) and used as received. Toluene was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received.

Preparation of O-cCNC

In a typical procedure, cCNC (1 g) was dispersed in toluene (20 mL). Then, n-octyltrimethoxysilane (0.5 g) was added. The mixture was stirred at 110 °C with a condenser for 24 h. The final solid was separated by centrifugation and washed with toluene (3 × 15 mL) and ethanol (3 × 15 mL) before dried at 60 °C for 5 h.

Preparation of Pd/O-cCNC

A total of 50 mg PdCl₂ was dissolved in 10 mL ethanol and the mixture was sonicated for 30 min before catalysts preparation. A 100 mg amount of O-cCNC and 0.2

mL 5 mg/mL PdCl₂ solution was mixed and milled manually for 20 min in an agate mortar. The sample was kept for 24 h to achieve adsorption of the Pd ions on the surface of O-cCNC. Thereafter, 60 mg HCOONa was added to the powder mixture and ground for 30 min and kept for another 24 h. The as-prepared sample was washed repeatedly with distilled water (3 × 15 mL) and ethanol (3 × 15 mL) to remove unreacted PdCl₂ and sodium formate. The obtained sample (Pd/O-cCNC) was dried in vacuum oven at 25 °C for 12 h. Pd/cCNC was prepared with the same procedure.

Characterizations

Scanning electron microscopy (SEM) images were taken with a JSM-7800F SEM (JEOL, Tokyo, Japan). Transmission electron microscopy (TEM) images were taken using a FEI-Talos F200S microscope operating at 120 kv. A 5 mg sample was dispersed in 2 mL ethanol and sonicated for 5 min. Energy Dispersive X-ray Spectroscopic analysis (EDS) was performed with a JEM-2010(HR) TEM at 200kV. X-ray photoelectron spectroscopy (XPS) was performed on an AXIS-Ultra DLD (Kratos, Shimadzu, Japan) and calibrated by setting the C1 s peak to 284.80 eV. Surface wettability of the samples was investigated by the analysis of the water contact angles (WCA) on KRUSS DSA100 (Hamburg, Germany). Samples were directly compressed without the aid of binder. A drop of deionized water was then placed on it and imaged by camera. Microscope images of oil-in-water emulsions were obtained on optical microscope E200 (Nikon Instruments, China). ζ-potential was investigated using a dynamic light scattering instrument (Malvern Panalytical Ltd, NaNO-ZS ZEN3600, UK). The infrared spectra were analyzed using a Fourier-transform infrared spectrometer (FTIR) (Thermo Fisher, Nicolet iS5, USA)

Preparation and pH-responsiveness of the Pickering emulsion

20 mg O-cCNC was dispersed in 10 mL of water, then 2 mL of toluene was added. The mixture was emulsified in a homogenizer (HR-6B) at a shear rate of *ca.* 25000 s⁻¹ to obtain an emulsion. The pH-responsiveness of the emulsion was verified by adding 1 M NaOH and HCl aqueous solutions alternately.

Hydrogenation Reaction

Hydrogenation of nitrobenzene was chosen as the model reaction to test catalysts activity of Pd/O-cCNC with H₂ as hydrogen donor. Typically, 0.2 mmol nitrobenzene, 35 mg Pd/O-cCNC and 3 mL deionized water were added to a Schlenk tube and then purged with H₂ four times. The reaction was allowed to proceed for 1 h at room temperature. After reaction, the Pickering emulsion was demulsified through addition of 1M NaOH solution. The organic phase was diluted with ethyl acetate and analyzed by GC-MS.

RESULTS AND DISCUSSION

O-cCNC Characterization and its pH-responsive Emulsion

Initially, the morphology of pristine cCNC and O-cCNC was characterized by SEM. As shown in Fig. 1a, there were no rod- or needle-shaped structures of cCNC; rather, sheet-like structures were observed in its SEM image, which might be because of aggregation of cCNC during the drying process. The introduction of alkyl groups seemed to have no obvious influences on the morphology of cCNC (Fig. 1b).

Figure 1c shows the FTIR spectra of cCNC and O-cCNC. The peaks at 3330, 1587, and 2920 cm^{-1} were attributed to the stretching vibration of OH groups, $-\text{COOH}$ groups, and C–H groups, separately. Compared with cCNC, the O-cCNC showed a new peak at 798 cm^{-1} , which was attributed to bending vibration of Si–O groups, implying that silylated cCNC were successfully prepared.

The ζ -potentials of cCNC and O-cCNC are presented in Fig. 2d. Both cCNC and O-cCNC suspensions exhibited negative charge. No obvious difference in ζ -potential was detected. Since pH played an important role in the stabilization of Pickering emulsion in this work, O-cCNC suspension at different pH was also studied. As shown in Fig 2d, under alkaline condition, the ζ -potential of O-cCNC decreased from -24.3 mV to -40.77 mV. After neutralization with HCl, the ζ -potential of O-cCNC was back to -25.87 mV.

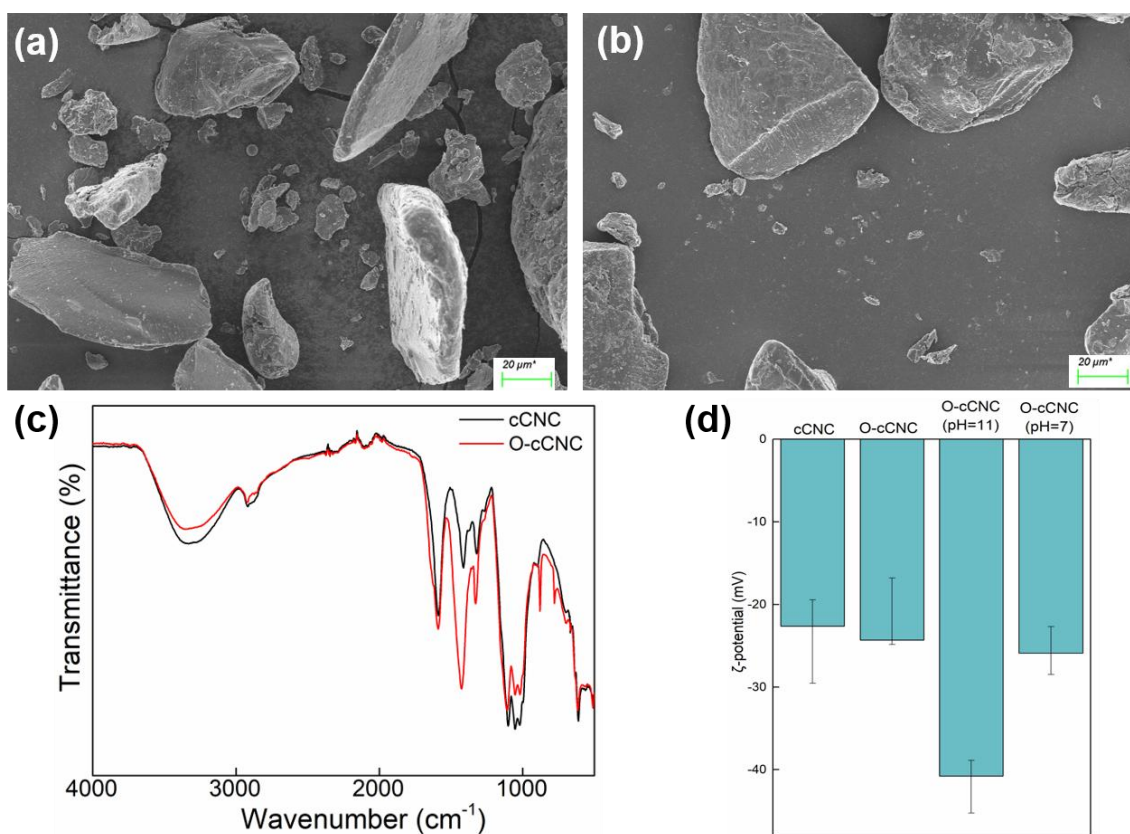


Fig. 1. SEM images of cCNC (a), O-cCNC (b); (c) FT-IR spectrum of cCNC, cCNC and (d) ζ -potential of cCNC, O-cCNC, O-cCNC (pH =11), O-cCNC (pH= 7)

Furthermore, the surface wettability of cCNC and O-cCNC was quantified by the water contact angle (WCA). As shown in Fig. 2(a) and (b), it could be found that the contact angle of O-cCNC increased from 52° to 72° , which was attributed to the successful hydrophobic modification. Notably, the WCA value was smaller than 90° , suggesting the preferred oil-in-water emulsions over the modified cCNC.

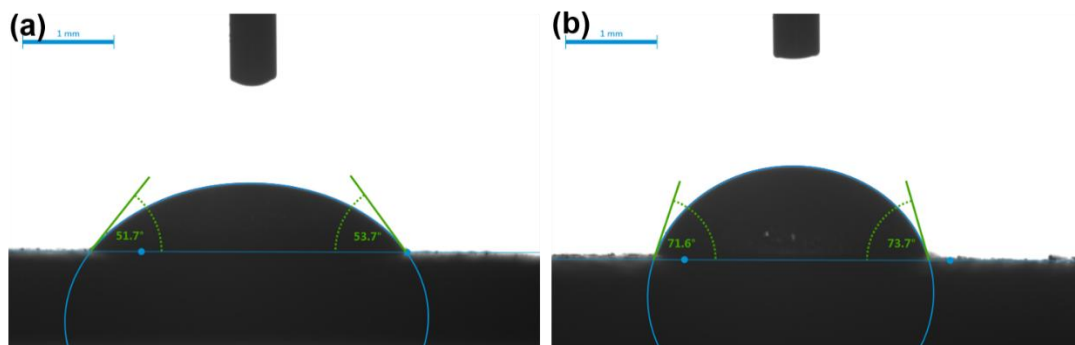


Fig. 2. WCAs of water on the surface of cCNC (a) and O- cCNC (b)

The emulsion properties of cCNC and O-cCNC were further examined by testing their emulsifying capacity in the toluene/water system. The obtained emulsions were stored in sample bottles and sealed carefully. An obvious difference in the behaviour of cCNC and O-cCNC was observed. O-cCNC gave a highly dispersed Pickering emulsion, and the emulsion was stable for at least 12 h with slight phase separation (Fig. 3a and 3b). Meanwhile, emulsion stabilized by cCNC was unstable and rapid phase separation was observed, indicating the presence of alkyl groups enhances the hydrophobicity of cCNC and is beneficial to the formation of emulsions. Stable Pickering emulsions make O-cCNC the desirable support for Pickering interfacial catalysts. The morphology of O-cCNC stabilized emulsion was characterized by optical microscope, as shown in Fig. 3c. The optical micrograph exhibited well-defined oil-in-water droplets with an average diameter of 60 μm .

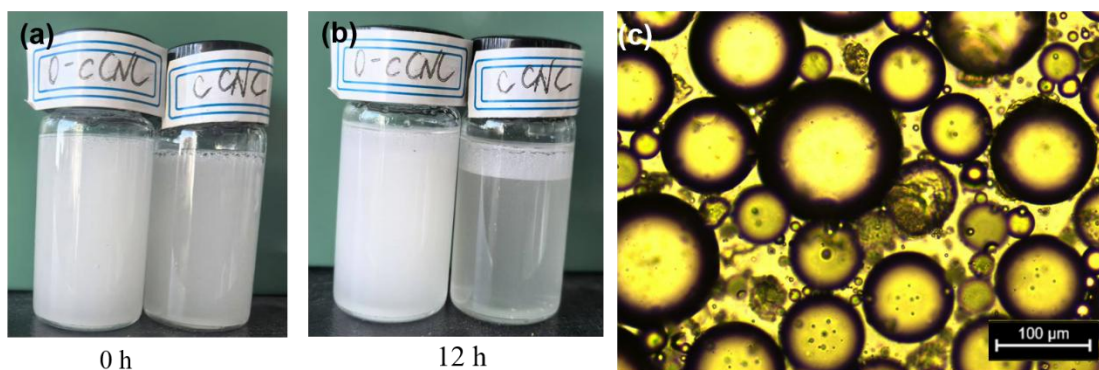


Fig. 3. Digital photos of Pickering emulsions stabilized by cCNC and O-cCNC taken at (a) 0 h and (b) 12 h; (c) Optical micrograph image of O-cCNC stabilized Pickering emulsion

The pH-responsiveness of the obtained Pickering emulsion was examined. When NaOH solution was added to adjust pH to 11, the emulsion quickly demulsified with shaking and separated into oil and water after standing (Fig. 4a). O-cCNC migrated to the bottom aqueous phase due to increased hydrophilicity upon deprotonation of the attached carboxylic acid groups under alkaline condition, which is in consist with Fig. 1d. Deprotonation of carboxylic acid groups led to a decrease of ζ -potential. A stable emulsion could be regenerated upon addition of HCl solution to adjust pH to 7 and subsequent homogenization. Figure 4b shows that the emulsion still had high stability after adjusting the pH for 6 cycle, and it can be seen that the particle size distribution of the emulsion was almost unchanged before and after the stimulus. The pH-responsiveness of cCNC

stabilized Pickering emulsion was also examined. Although c cannot form stable emulsion, the pH-responsive behavior was also observed, indicating the pH-responsiveness is mainly due to COOH groups in cCNC and that silylation has little effect on COOH groups and pH-sensitivity.

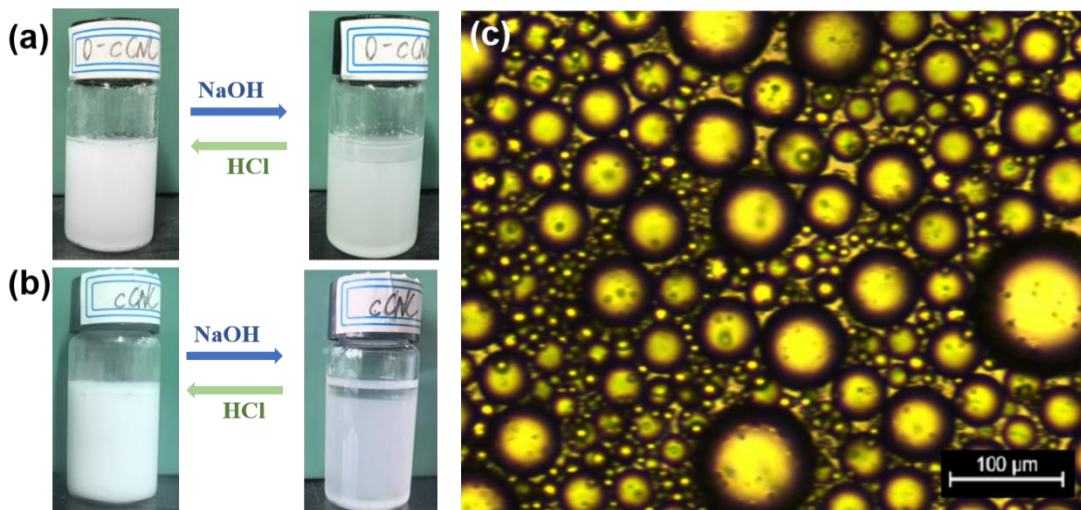


Fig. 4. Digital photos of an emulsion before and after alternately adding NaOH and HCl aqueous solutions stabilized by (a) O-cCNC and (b) cCNC; (c) Optical micrograph of emulsion stabilized by O-cCNC after alternately adding NaOH and HCl aqueous solutions for 6 cycles.

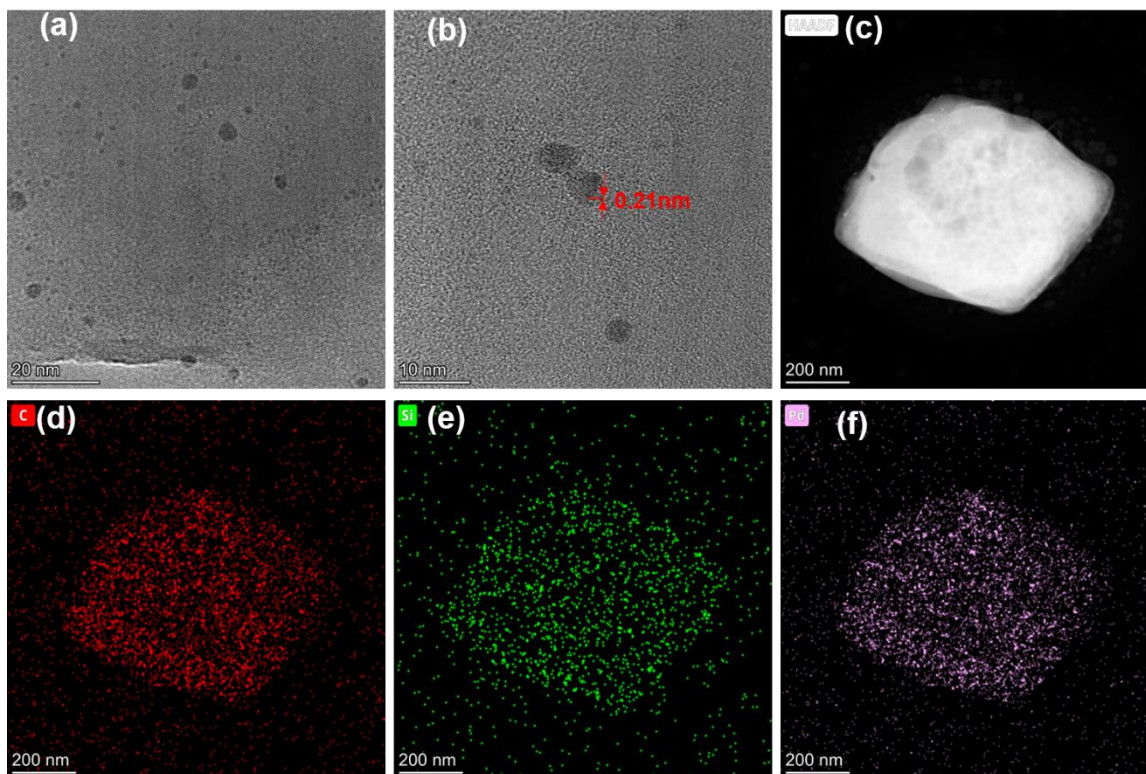


Fig. 5. TEM images (a, b) and element mapping images (c-f) of Pd/O-cCNC

The Pd/O-cCNC were characterized by TEM. As shown in Fig. 5a, the Pd NPs were spherical with average diameters of about 3 nm. Further high-resolution TEM analysis revealed a highly integrated nanostructure of Pd NPs (Fig. 5b). The well-resolved lattice spacing of 0.20 nm corresponding to the (111) of the metallic Pd can be perceived. The elemental mappings (Fig. 5c-f) revealed that Si and Pd atoms were uniformly distributed on the surface of O-cCNC. Therefore, it can be confirmed that Pd NPs supported on silylated cCNC had been successfully prepared.

The Pd/O-cCNC was further characterized by X-ray photoelectron spectroscopy (XPS). The Pd 3d region spectrum revealed that Pd⁰ and Pd²⁺ coexisted on the surface of the catalyst and mainly were in the metallic state (Fig. 6b). The peaks at 335.3 eV and 340.1 eV were assigned to the Pd 3d_{5/2} and Pd 3d_{3/2} transitions, respectively. The C 1s XPS spectra consists of four peaks located at 284.8eV, 286.5 eV, 288.2 eV, and 289.7eV corresponding to C-C, C-Si-O, C-O, and O=C-O species, respectively (Fig. 6a).

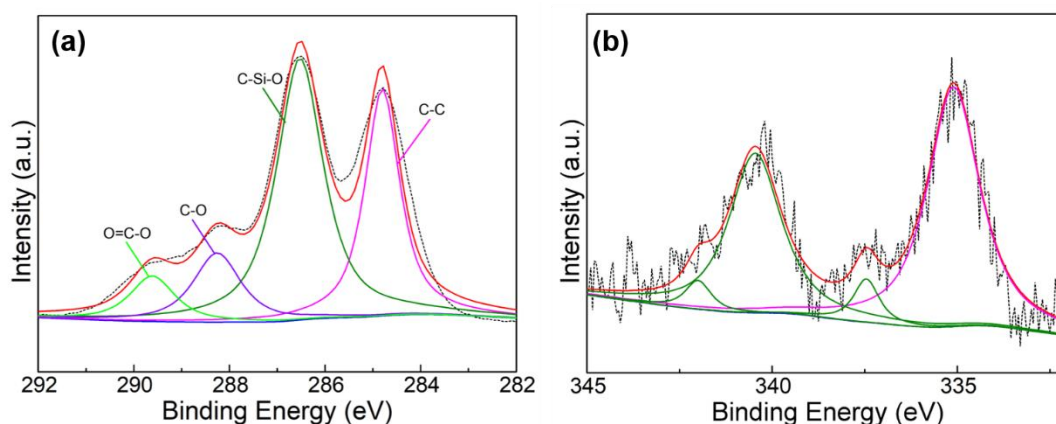


Fig. 6. (a) XPS C 1s spectra of Pd/ O-cCNC; (b) XPS Pd 3d spectra of Pd/ O-cCNC

Emulsion Interfacial Catalysis with Pd/O-CNC

The applicability of the authors' Pickering interface catalyst was further evaluated in hydrogenation of nitrobenzene. Nitrobenzene is insoluble in the aqueous phase and Pickering interfacial catalyst would activate the reaction at the interface. Upon dispersing nitrobenzene in the water phase containing Pd/O-cCNC, the catalyst rapidly adsorbed onto the nitrobenzene-water interface. After stirring for a short time (5 min), nitrobenzene-in-water Pickering emulsion was formed.

Nitrobenzene-in-water droplets with an average diameter of 40 μm were observed *via* optical microscope (Fig. 7a). A total of 95% conversion of nitrobenzene could be achieved over Pd/O-cCNC in 1 h at room temperature (Fig. 7b). When Pd/cCNC with the same Pd amount was applied in the hydrogenation of nitrobenzene, only 69% yield of aniline was achieved (Fig. 7b). It is obvious that the hydrophobic group on cCNC surface played an important role in accelerating the catalytic reaction in the interface between organic and water.

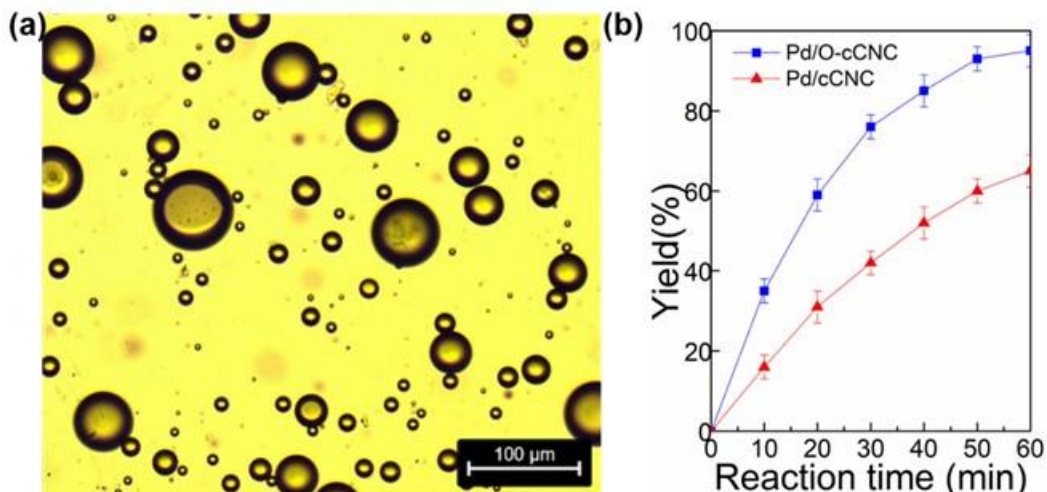


Fig. 7. (a) Optimal micrograph image of nitrobenzene in water emulsion, (b) plotting of aniline yield as a function of reaction time

The recyclability of Pd/O-cCNC was further investigated. After reaction, quick phase separation was realized by adding NaOH solution and adjusting the pH to 11. Organic reactant and product were separated. The aqueous phase was then neutralized with HCl solution until pH = 7 and used in the next cycle. Even after 7 repetitive hydrogenation reactions, the Pd/O-cCNC still could maintain high activity (Fig. 8a). Furthermore, Pickering emulsion stabilized by reused Pd/O-cCNC was characterized, droplets with sizes of 40 μm were observed (Fig. 8b), indicating the reaction procedure made almost no effect on the emulsion capacity of Pd/O-cCNC. Pd/O-cCNC after 7 runs was characterized by TEM, a slight increase in Pd NPs size and was observed (Fig. 8c), which was believed to be the main reason for the slight deactivation of the catalyst.

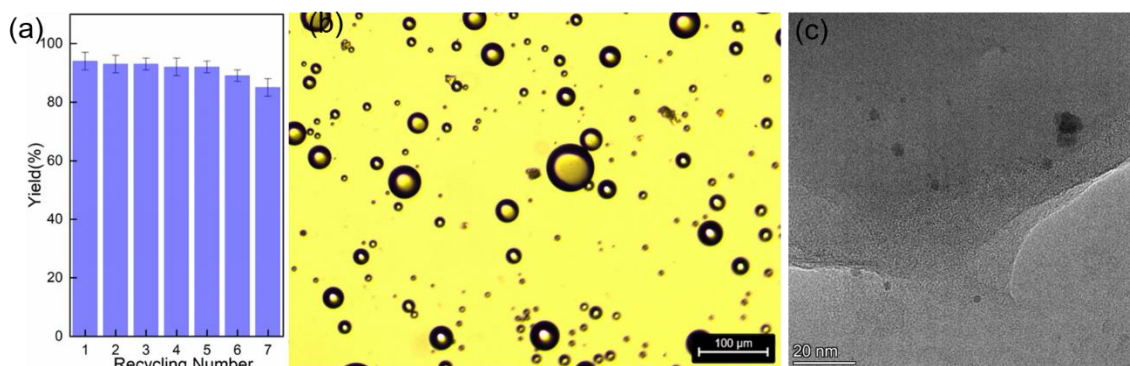


Fig. 8. (a) Recycling performance of Pd/O-cCNC with a lower amount of catalyst, (b) optimal micrograph image of oil-in-water emulsion stabilized by reused Pd/O-cCNC, and (c) TEM image of reused Pd/O-cCNC

CONCLUSIONS

1. A pH-responsive Pickering interfacial catalyst was successfully constructed *via* surface modification of carboxylated cellulose nanocrystals and sequential deposition of Pd nanoparticles (NPs).
2. The pH-sensitivity of COOH groups allow the emulsion to be separated into oil and water quickly under alkaline condition and thus allows recovery of the products and catalysts. By adding NaOH, demulsifying behaviour was observed due to deprotonation the carboxylic acid moieties and emulsifying behavior could be achieved by adding HCl.
3. The obtained Pickering interfacial catalyst exhibited remarkable activity in hydrogenation reaction of nitrobenzene in aqueous phase.

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REFERENCES CITED

- Chang, F., Vis, C. M., Ciptonugroho, W., and Bruijninx, P. C. A. (2021). "Recent developments in catalysis with Pickering emulsions," *Green Chemistry* 23(7), 2575-2594. DOI: 10.1039/D0GC03604H
- Chen, C., Zhang, L., Wang, N., Sun, D., and Yang, Z. (2023). "Janus composite particles and interfacial catalysis thereby," *Macromolecular Rapid Communications* 44(20), article ID 2300280. DOI: 10.1002/marc.202300280
- Dan, H., Zhao, H., Gao, Y., Zhang, B., Xu, X., Yue, Q., Leiviskä, T., Jin, B., Chen, B., and Gao, B. (2024). "Accelerated selective oxidation of benzyl alcohol to benzaldehyde *via* a self-catalyzed Pickering emulsion microreactor," *Journal of Materials Chemistry A* 12(37), 25381-25392. DOI: 10.1039/D4TA04195J
- Gong, Y., Li, T., Krainov, A. A., Voronin, D. V., Semenov, A. P., Dubinich, V. N., Panchenko, A. A., and Vinokurov, V. A. (2022). "Functional materials based on carboxylated nanofibrillar cellulose," *Chemistry and Technology of Fuels and Oils* 58(5), 809-814. DOI: 10.1007/s10553-022-01456-7
- Guo, J.-L., Sun, Q.-Q., Liu, Z.-Q., Wang, F.-X., Fu, T., Liu, Y., and Ying, A. (2024). "An intelligent dual stimuli-responsive Pickering emulsion for highly efficiently producing waste frying oil-based biodiesel," *Journal of Cleaner Production* 436, article ID 140638. DOI: 10.1016/j.jclepro.2024.140638
- Guo, X., Gao, H., Zhang, J., Zhang, L., Shi, X., and Du, Y. (2021). "One-step electrochemically induced counterion exchange to construct free-standing

- carboxylated cellulose nanofiber/metal composite hydrogels,” *Carbohydrate Polymers* 254, article ID 117464. DOI: 10.1016/j.carbpol.2020.117464
- Li, Z., Shi, Y., Ding, Y., Xiong, D., Li, Z., Wang, H., Qiu, J., Xuan, X., and Wang, J. (2024). “Zr-Based MOF-stabilized CO₂-responsive Pickering emulsions for efficient reduction of nitroarenes,” *Langmuir* 40(6), 3133-3141. DOI: 10.1021/acs.langmuir.3c03564
- Li, Z., Shi, Y., Zhu, A., Zhao, Y., Wang, H., Binks, B. P., and Wang, J. (2021). “Light-responsive, reversible emulsification and demulsification of oil-in-water Pickering emulsions for catalysis,” *Angewandte Chemie International Edition* 60(8), 3928-3933. DOI: 10.1002/anie.202010750
- Liu, Z.-Q., Guo, J.-L., Liang, R.-H., Wang, F.-X., Li, Z.-K., Liu, Y., and Ying, A. (2024). “Two birds with one stone: A magneto-optical dual-stimuli-responsive intelligent Pickering emulsion for efficient conversion of glucose to 5-hydroxymethylfurfural,” *Chemical Engineering Journal* 479, article ID 147757. DOI: doi.org/10.1016/j.cej.2023.147757
- Lu, X., Li, S., Wang, L., Huang, S., Liu, Z., Liu, Y., and Ying, A. (2022). “Novel photic and magnetic double responsive Pickering interfacial solid catalysts for biodiesel production,” *Fuel* 310, article ID 122318. DOI: 10.1016/j.fuel.2021.122318
- Luo, R., Dong, J., and Luo, Y. (2020). “pH-responsive Pickering emulsion stabilized by polymer-coated silica nanoaggregates and applied to recyclable interfacial catalysis,” *RSC Advances* 10(69), 42423-42431. DOI: 10.1039/D0RA07957J
- Ma, Q., Zhou, H., Shao, X., Chen, J., Cheng, Y., Chen, M., Jiang, Y., Chen, X., Ke, Q., Wang, Y., *et al.* (2024). “Pickering emulsions stabilized by linear amphiphilic polymers for enhancing the selective oxidation of cinnamyl alcohol,” *ACS Applied Polymer Materials* 6(16), 10083-10089. DOI: 10.1021/acsapm.4c02214
- Ma, S., Zong, W., and Han, X. (2021). “Magnetic-responsive Pickering emulsion and its catalytic application at the water–oil interface,” *New Journal of Chemistry* 45(8), 3974-3980. DOI: 10.1039/D0NJ05875K
- Meng, W., Sun, H., Mu, T., and Garcia-Vaquero, M. (2023). “Chitosan-based Pickering emulsion: A comprehensive review on their stabilizers, bioavailability, applications and regulations,” *Carbohydrate Polymers* 304, article ID 120491. DOI: 10.1016/j.carbpol.2022.120491
- Morais, J. P., Rosa, M. D., Brito, E. S., Azeredo, H. M., and Figueirêdo, M. C. (2023). “Sustainable Pickering emulsions with nanocellulose: Innovations and challenges,” *Foods* 12, article ID 3599. DOI: 10.3390/foods12193599
- Pei, X., Song, W., Zhao, Y., and Li, Z. (2024). “CO₂-switchable amidine-modified ZIF-90-stabilized Pickering emulsions for controllable Knoevenagel condensation reactions,” *Molecular Systems Design & Engineering* 9(3), 278-285. DOI: 10.1039/D3ME00167A
- Qi, L., Zhou, Y.-j., Luo, Z.-g., Gao, Q.-y., and Shi, Y.-C. (2023). “Facile synthesis of lipase-loaded starch nanoparticles as recyclable biocatalyst in Pickering interfacial systems,” *Carbohydrate Polymers* 299, article ID 120203. DOI: 10.1016/j.carbpol.2022.120203
- Richards, K. D., and Evans, R. C. (2022). “Light-responsive Pickering emulsions based on azobenzene-modified particles,” *Soft Matter* 18(31), 5770-5781. DOI: 10.1039/D2SM00697A
- Tiban Anrango, B. A., Naiya, M. M., Van Dongen, J., Matich, O., Whitby, C. P., and Chen, J. L. Y. (2024). “Nanoprecipitation to produce hydrophobic cellulose

- nanospheres for water-in-oil Pickering emulsions,” *Cellulose* 31(10), 6225-6239.
DOI: 10.1007/s10570-024-05983-w
- Wang, H.-H., Li, F., Yao, B.-J., and Dong, Y.-B. (2024). “Pd NP-loaded covalent organic framework for pH-switched Pickering emulsion catalytic dichlorination,” *Chemical Communications* 60(25), 3445-3448. DOI: 10.1039/D3CC05982K
- Wang, Q., Liu, S., Chen, H., Liu, J., Liu, H., and Zhu, Q. (2023). “Carboxylated cellulose silica hybrid beads for efficient dye removal,” *BioResources* 18(2), 4104-4115. DOI: 10.15376/biores.18.2.4104-4115
- Wu, M., Xue, Z., Wang, C., Wang, T., Zou, D., Lu, P., and Song, X. (2024). “Smart antibacterial nanocellulose packaging film based on pH-stimulate responsive microcapsules synthesized by Pickering emulsion template,” *Carbohydrate Polymers* 323, article ID 121409. DOI: 10.1016/j.carbpol.2023.121409
- Xiao, Z., Wang, L., Lv, C., Guo, S., Lu, X., Tao, L., Duan, Q., Yang, Q., and Luo, Z. (2020). “Preparation and characterization of pH-responsive Pickering emulsion stabilized by grafted carboxymethyl starch nanoparticles,” *International Journal of Biological Macromolecules* 143, 401-412. DOI: 10.1016/j.ijbiomac.2019.10.261
- Yokota, S., Kamada, K., Sugiyama, A., and Kondo, T. (2019). “Pickering emulsion stabilization by using amphiphilic cellulose nanofibrils prepared by aqueous counter collision,” *Carbohydrate Polymers* 226, Article ID 115293. DOI: 10.1016/j.carbpol.2019.115293
- Zhang, Q., Zhang, X., Yan, N., and Chen, K. (2023). “Pickering emulsion stabilized by temperature-sensitive PS@PNIPA nanoparticles as microcontainers,” *Polymer* 268, article ID 125710. DOI: 10.1016/j.polymer.2023.125710
- Zhang, Y., Luo, P., Qi, J., Lu, H., Wang, L., and Wu, Y. (2024a). “A pH-switchable Pickering emulsion synergistically stabilized by nanoparticles as an efficient medium for utilizing ammonia borane for organic conversion,” *New Journal of Chemistry* 48(18), 8371-8385. DOI: 10.1039/D4NJ00138A
- Zhang, J., Wu, Q., Li, W., and Negulescu, I. (2024b). “Renewable resources derived cellulose nanocrystal stimuli responsive Pickering emulsions,” *BioResources* 19(4), 9905-9922. DOI: 10.15376/biores.19.4.Zhang2
- Zhang, Z., Peng, B., Zhang, Y., Xiong, J., Li, J., and Liu, J. (2024c). “Switchable Pickering emulsions stabilized via synergistic nanoparticles–superamphiphiles effects and rapid response to CO₂/N₂,” *Langmuir* 40(3), 1604-1612, DOI: 10.1021/acs.langmuir.3c02206

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