Palladium nanoparticles anchored on amphiphilic Janus–type nano-cellulose for Pickering interfacial catalysis

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1. Experimental section

1.1 Materials and reagents

All chemical reagents are obtained from commercial suppliers and used without further purification. α-cellulose with an average length of 60 μm purchased from Meryer was used as starting material to prepare CNC.

1.2 Characterizations

TEM images were taken using a PHILIPS Tecnai 12 microscope operating at 120kv. 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 1 s peak to 284.80 eV. Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV. Surface wettability of the samples was investigated by the analysis of the water contact angles (WCA) on TX500TM (Kono Corp.) 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 sulfide-in-water emulsions were obtained on BX53M (Olympus Corp.).

1.3 Preparation of CNC

The micro-cellulose were hydrolyzed using 50% v/v sulfuric acid solutions at 35 °C for 30 minutes. The acid/cellulose ratio of 25:1 (mL/g cellulose) was maintained. After the hydrolysis, the reaction was stopped by the addition of deionized ice water. Subsequently, the resulting suspension was neutralized with 1M NaOH before centrifuged at 9000 rpm for remove the nanocrystals from the solution and washed with deionized water. The obtained suspension was then freeze-dried on a freeze-dryer for 48h.

1.4 Preparation of NC-CNC

Wax@CNC were synthesized on the basis of a wax-in-water emulsion using cetyltrimethylammonium bromide (CTAB) as a surfactant. CNC (0.25 g) and paraffin wax (2.5 g) were added to the aqueous solution (20 mL) of 0.72 $mmol.L^{-1}$ CTAB. The resulting mixtures were incubated at 75 °C for 0.5 h, and then vigorously stirred for 10 min. After being rapidly cooled to room temperature, wax@ CNC droplets were obtained. The wax droplets were filtered, washed with deionized water to remove the excess and weakly attached CNC nanoparticles, and then dried at 25 °C under vacuum for 24 h.

The obtained dried wax@CNC (2.5 g) was dispersed in dry DMF (20 ml). The mixture was

cooled to 0 °C and NaH (300 mg) was added in two portions. After stirring for 30 min, $C_{16}H_{33}Br$ (300mg) was slowly added and the reaction mixture was warmed to room temperature. After stirring overnight, the reaction mixture was filtrated. Then, chloroform was used to dissolve the paraffin wax at 40 °C, thereby releasing the CNC nanoparticles. After centrifugation, the residue was washed with chloroform and anhydrous ethanol for several times, and dried under vacuum at 40 °C for 24 h. The obtained samples were denoted as NC-CNC.

1.5 Preparation of Pd/NC-CNC and Pd/ CNC

50 mg $PdCl_2$ was dissolved in 10 ml ethanol and the mixture was sonicated for 30 mins before catalysts preparation. A 100 mg amount of NC-CNC and 0.2ml 5mg/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 the Pd ions on the surface of the Cell. Thereafter, 60 mg of ascorbic acid was added to the powder mixture and grounded for 30 min and kept for another 24h. The as-prepared samples were washed repeatedly with distilled water (3 × 15 ml) and ethanol (3 × 15 ml) to remove unreacted $PdCl_2$ and sodium formate. The obtained samples (Pd/NC-CNC) were dried in in vacuum oven at 25 °C for 12 h. Pd/CNC was prepared with the same procedure.

1.6 Catalytic reduction of nitrobenzene

Hydrogen was chosen as hydrogen donor for the hydrogenation of nitroarenes. The hydrogenation reactions were carried out in a Schlenk tube. Typically, nitrobenzene (0.2 mmol) and catalyst (35mg) were dispersed into water, then the Schlenk tube was purged with H_2 four times to replace air. Then the mixture was stirred at room temperature for a desired period. After reaction, catalyst was separated from the reaction mixture by centrifugation and washed with ethyl acetate (3 × 15 ml), deionized water (3 × 15 ml) and then used in the next cycle. Remained mixture was extracted by ethyl acetate. The product and unreacted reactant were analyzed by GC–MS. The catalysts were separated by centrifugation.

For the reusability tests of the catalyst, 17.5mg catalyst was used in each run.

1.7 Suzuki reaction

A mixture of bromobenzene (0.2 mmol), phenylboronic acid (0.23mmol), and K_2CO_3 (0.4mmol) in 3mL of deionized water and 70mg catalysts was degassed with Ar and added to a 15mL flask. The reaction mixture was heated up to 80°C and the reaction was allowed for 4h. Bromobenzene reacted with phenylboronic acid by following the Suzuki reaction, and the reaction

yield was determined s by GC.

For the reusability tests of the catalyst, 35 mg catalyst was used in each run.

1.8 Pickering emulsion stabilization tests

1.0 mg Pd/NC-CNC, 4.0 mL H_2O and 1.0 mL hexane or organic reactants were mixed and sonicated for 5 mins to form an emulsion. The system was then set still for observation. The Pickering emulsion produced was observed with a bright field microscope. The emulsion drop diameter was measured by analyzing the microscope images.

2. SEM images of CNC and NC-CNC

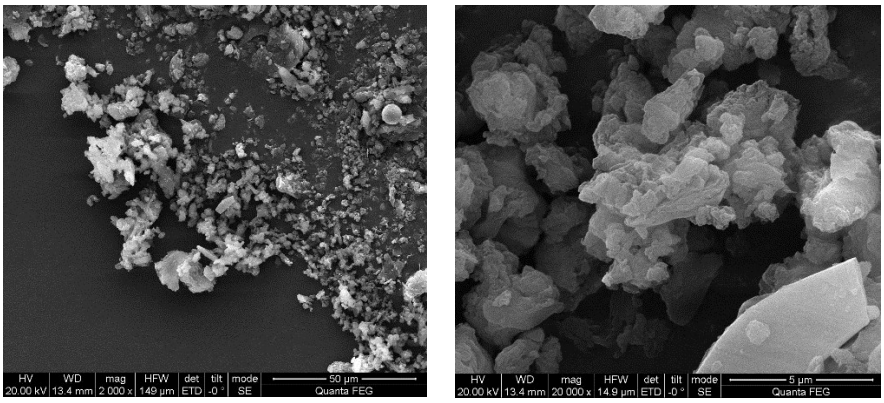
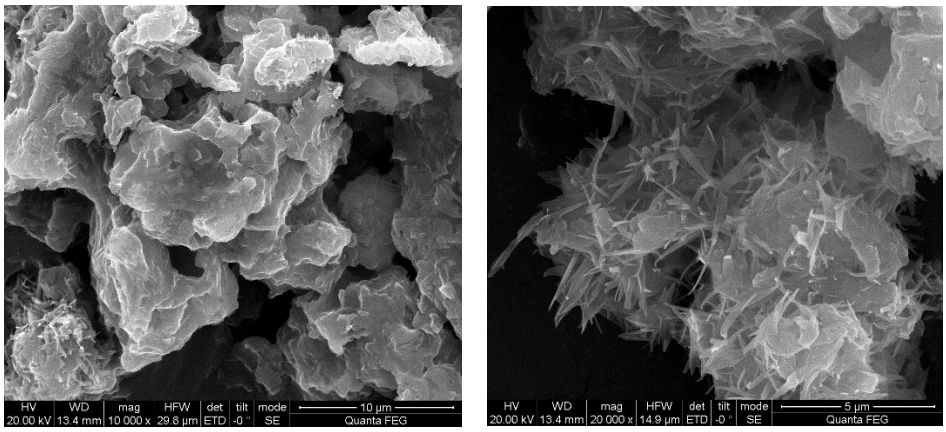


Figure S1 SEM images of CNC



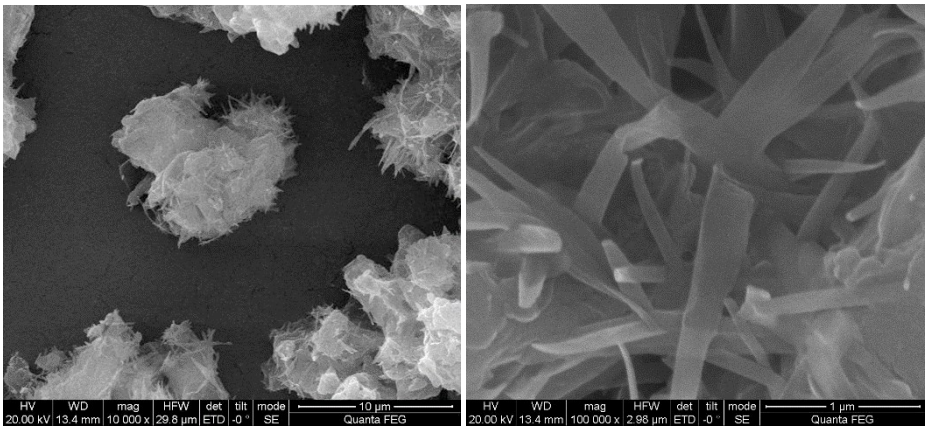


Figure S2 SEM images of NC-CNC

3. TEM images of CNC and NC-CNC

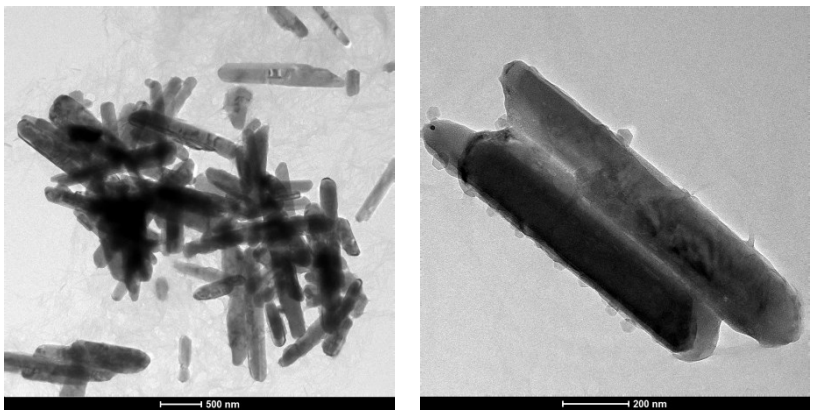


Figure S3 TEM images of CNC

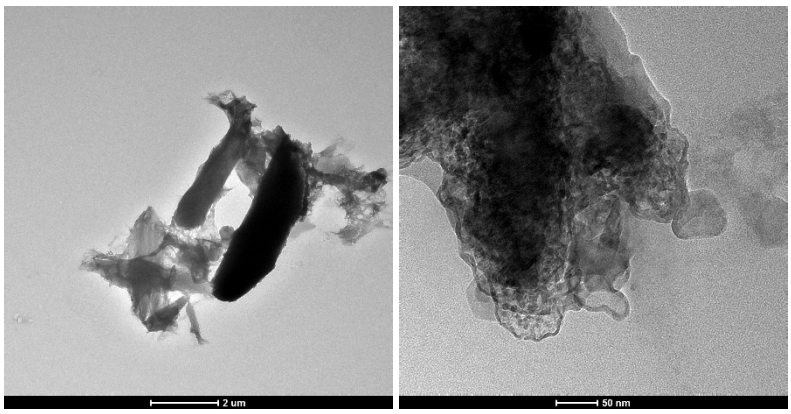


Figure S4 TEM images of NC-CNC

4. TEM images of Pd/NC-CNC

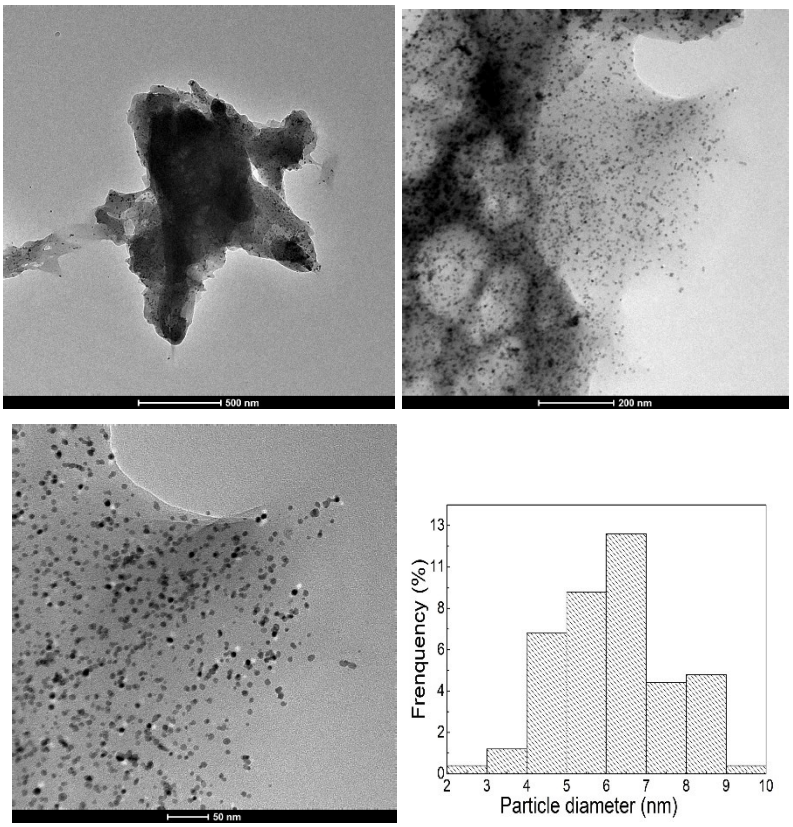


Figure S5 TEM images of Pd/NC-CNC

5. XPS spectrum of Pd/NC-CNC

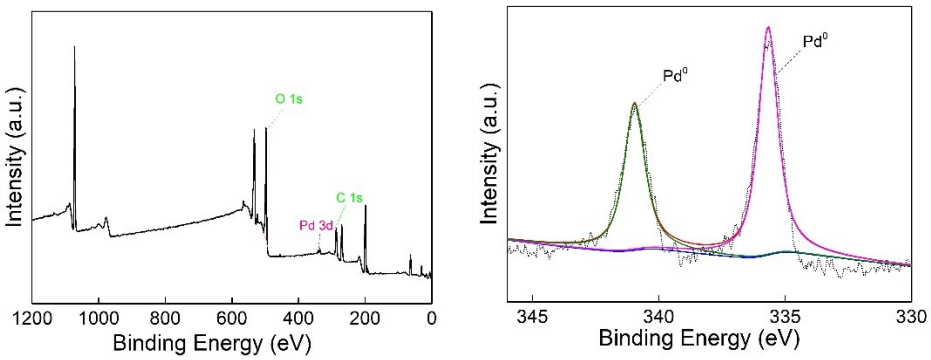


Figure S6 (a) Full-range XPS spectrum and (b) Pd 3d spectrum of Pd/NC-CNC

6. TEM images of Pd/NC-CNC after reused for 8 times in reduction reaction

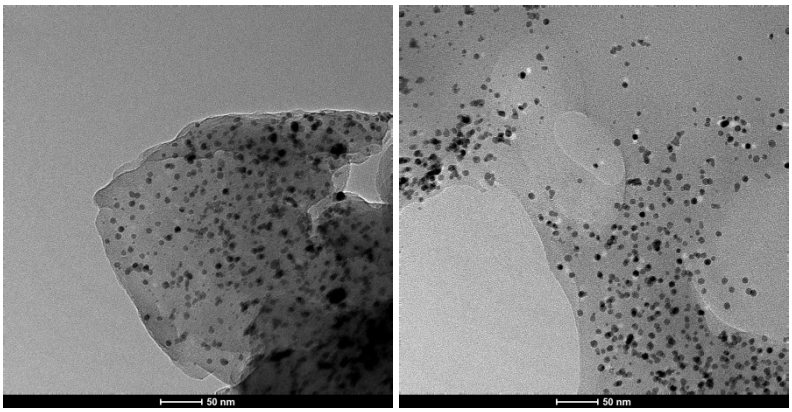


Figure S7 TEM images of Pd/NC-CNC after reused for 8 times in reduction reaction

7. XPS spectrum of Pd/NC-CNC after reused for 8 times in reduction reaction

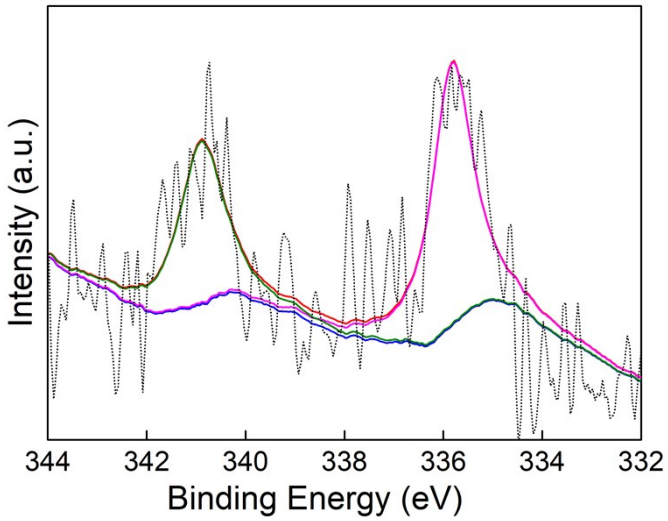


Figure S8 Pd 3d spectrum of Pd/NC-CNC after reused for 8 times in reduction reaction

8. Optimal images of Pickering emulsion stabilized by Pd/NC-CNC after reused for 8 times in reduction reaction

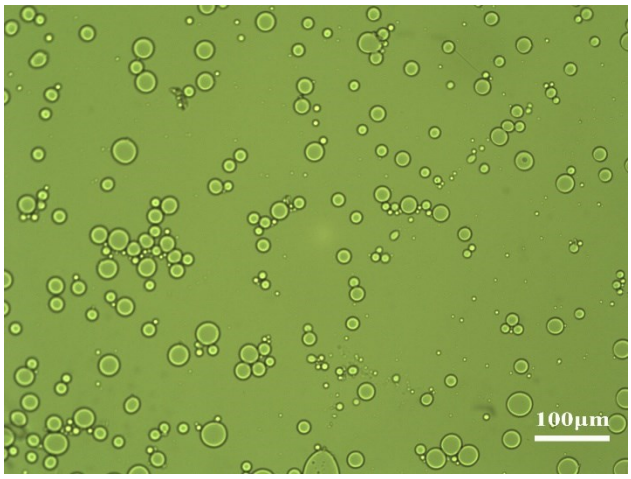


Figure S9 Optimal images of Pickering emulsion stabilized by Pd/NC-CNC after reused for 8

times in reduction reaction

9. TEM images of Pd/NC-CNC after reused for 6 times in Suzuki reaction

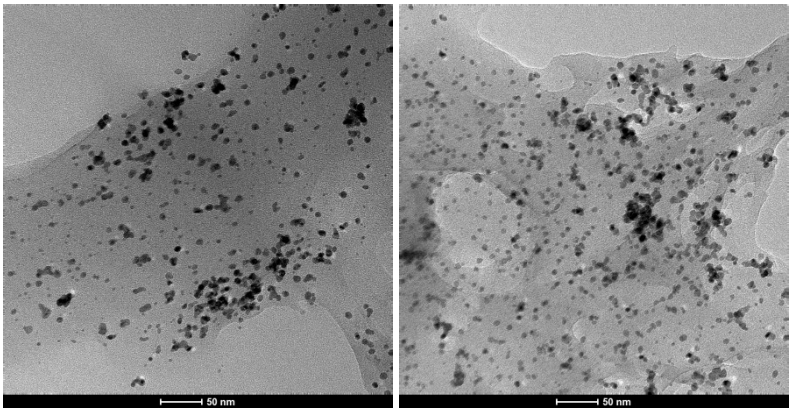


Figure S10 TEM images of Pd/NC-CNC after reused for 6 times in Suzuki reaction

10. XPS spectrum of Pd/NC-CNC after reused for 6 times in Suzuki reaction

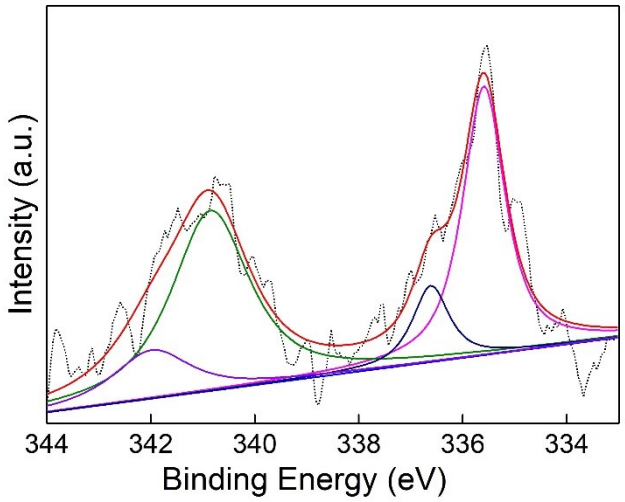


Figure S11 Pd 3d spectrum of Pd/NC-CNC Pd/NC-CNC after reused for 6 times in Suzuki reaction

11. Optimal images of Pickering emulsion stabilized by Pd/NC-CNC after reused for 6 times in Suzuki reaction

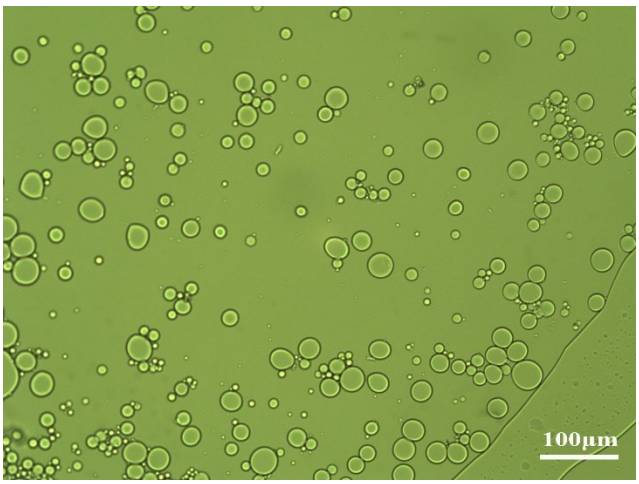


Figure S12 Optimal images of Pickering emulsion stabilized by Pd/NC-CNC after reused for 6 times in Suzuki reaction

12. ICP results of Pd leaching in reaction solutions after each run.

Table S1. Reduction reduction

Run	Pd content (mg/L)
1	0.58
2	0.42
3	0.24
4	0.15
5	0.21
6	0.30
7	0.18
8	0.14
9	0.27

Table S2. Suzuki coupling reaction

Run	Pd content (mg/L)
1	1.20
2	0.69
3	0.32
4	0.44

5	0.21
6	0.33
7	0.14