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Supporting Information

Palladium nanoparticle loaded β-cyclodextrin monolith as flow reactor for concentration enrichment and conversion of pollutants based on molecular recognition

Shunsuke Mizuno[a], Taka-Aki Asoh[a*], Yoshinori Takashima[bc], Akira Harada[d], and Hiroshi Uyama[a*]

[a.] Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka, 565-0871, Japan.
[b.] Department of Macromolecular Science, Graduate School of Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan.
[c.] Institute for Advanced Co-Creation Studies, Osaka University, 1-1 Machikaneyamacho, Toyonaka, Osaka 560-0043, Japan.
[d.] The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

Materials and methods

Materials

Monochlorotriazine-modified β-cyclodextrin derivative (MCT-β-CD, containing 12.7 eq. NaCl, Degree of substitution value: 0.63) was provided by CycloChem Co., Ltd. Polyethyleneimine (PEI, molecular weight: 1,800), palladium acetate ($Pd(OAc)_2$), sodium borohydride ($NaBH_4$), and ammonium formate were purchased from FUJIFILM Wako Pure Chemical Corporation. 4-nitrophenol (4-NP) was purchased from Tokyo Chemical Industry Co., Ltd. Other reagents and all solvents were used as received.

Monolith preparation and catalyst immobilization

The β-CD cross-linked polymer monolith was synthesized through a cross-linking induced phase separation method according to our previously reported method[1] with some modification. MCT-β-CD (160 mg) and PEI (20 mg) were completely dissolved in deionized water (total volume: 800 μL). After bubble removal by sonication, the solution was poured into a polytetrafluoroethylene (PTFE) tube (inner diameter: 8.0 mm), and then cured at 10 °C for 72 h. The obtained white hydrogel was soaked in water, ethanol, and *n*-hexane, consecutively, and any solvents were removed by vacuum drying to produce a monolith (CD monolith, diameter: 6.4 mm, height: 12.5 mm). The monolith column was prepared in heat-shrinkable tubes (THT tube, DENKA Electron). The palladium catalyst was immobilized on a CD monolith by the following $Pd(OAc)_2$ adsorption method. The dried CD monolith column was connected to a peristaltic pump, and then acetone was run for 5 min at a flow rate of 5 mL/min to completely soak the CD monolith. $Pd(OAc)_2$/acetone solution (25 μg/mL, 20 mL) was passed through the

monolith for 30 min at a flow rate of 5 mL/min using a circulation flow system (Fig. S1). Then, the same $Pd(OAc)_2$ solution was prepared and flowed in the opposite direction in the same manner. After the adsorption of Pd(II) ions, pure acetone and water were passed through the monolith to remove excess $Pd(OAc)_2$, followed by 1 mg/mL of $NaBH_4$ aqueous solution for 10 min at a flow rate of 1 mL/min to form palladium nanoparticles (Pd-NPs) in the CD monolith (Pd-CD monolith). After Pd-NP formation, the monolith was washed with pure DI water at a flow rate of 2 mL/min until the eluate was neutral.

Characterization

A scanning electron microscope (SEM, Hitachi S-3000 N, Tokyo, Japan), operated at 15 kV, was used to observe the macroporous structure of the monoliths. The macropores of the monoliths were analyzed by an image analysis software (ImageJ) (total >300 counts). Pd-NPs, fixed in the Pd-CD monolith, were characterized by transmission electron microscopy (TEM, JEOL JEM-2010) with an accelerating voltage of 100 kV. To obtain accurate information about the Pd-NPs fixed in the Pd-CD monolith, an ethanol dispersion was made with finely crushed monolith powder, which was placed on a copper grid for TEM (NP-C15, Okenshoji, Co., Ltd.) observation. The loading palladium content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-8100). To prepare the sample, a monolith was dissolved in high-concentration nitric acid to obtain an aqueous solution, and the measurement was performed using a standard palladium solution. In the 4-NP reduction, detection of the reactant and substrate was performed using a high-performance liquid chromatography (HPLC, Agilent 1220 Infinity LC) system with a reverse phase column (TOSOH, TSKgel ODS-100V) and an ultraviolet detector. An ultraviolet-visible near-infrared

spectrophotometer (UV-vis-NIR, HITACHI, U-2810) was also used to calculate the amount of nitrophenol or aminophenol in the aqueous media.

4-nitrophenol reduction using molecular recognition

First, the Pd-CD monolith was connected to a peristaltic pump and fraction collector. 4-NP and ammonium formate as the hydrogen donors were dissolved in phosphate buffer (0.1 mol/L, pH 6.0) and adjusted to 0.1 mmol/L and 10 mg/mL, respectively. The solution flowed through the Pd-CD monolith for 20 min at a flow rate of 2 mL/min after passing the pristine phosphate buffer for 5 min at the same flow rate, and the eluate was collected every 4 mL continuously with a fraction collector. Every eluate sample was analyzed by HPLC to measure the elution amount of reactant and product. To reveal the scientific effect of host-guest interactions in a flow-based reaction system, 1-adamantanecarboxylic acid (Ad-COOH) was employed as the inhibitor for the 4-NP recognition by β-CD. Ad-COOH was added to the stock reaction solution to adjust the concentration to 20 eq. of the reactant, and the reduction reaction and analysis were carried out using the same rule.

Evaluation of adsorption ability by breakthrough curve

Phosphate buffer (0.1 mol/L, pH 6.0) was passed through the monolith for 5 min at a flow rate of 2 mL/min to soak the monolith, and then either 0.1 mmol/L 4-NP or 4-AP phosphate buffer solution flowed through at the same flow rate. The eluate was collected in a fixed amount with a fraction collector, and the elution amount of 4-NP and 4-AP was calculated using a UV-vis spectrophotometer (Hitachi, U-2810).

4-NP removal and remediation

The 4-NP adsorption and reduction were performed independently. A 4-NP aqueous solution (pH 5.0, adjusted by hydrochloric acid) was passed through the Pd-CD monolith at a flow rate of 2 mL/min. The 4-NP adsorption was performed in a volume of 10 mL at a concentration of 100 μmol/L or in 50 mL at 10 μmol/L. After the 4-NP adsorption, $NaBH_4$ aqueous solution (1 mg/mL) flowed through the 4-NP-adsorbed Pd-CD monolith to reduce the adsorbed 4-NP. The elution amount of 4-NP in the eluate was measured by HPLC. The reusability of the Pd-CD monolith was confirmed by stepwise 4-NP adsorption/reduction cycles. After the reduction of the adsorbed 4-NP (100 μmol/L), the Pd-CD monolith was washed with DI water until the eluate was neutral, and then the same adsorption/reduction process was again performed. The adsorption efficiencies and conversion rates were determined to evaluate the reusability of the flow reactor.

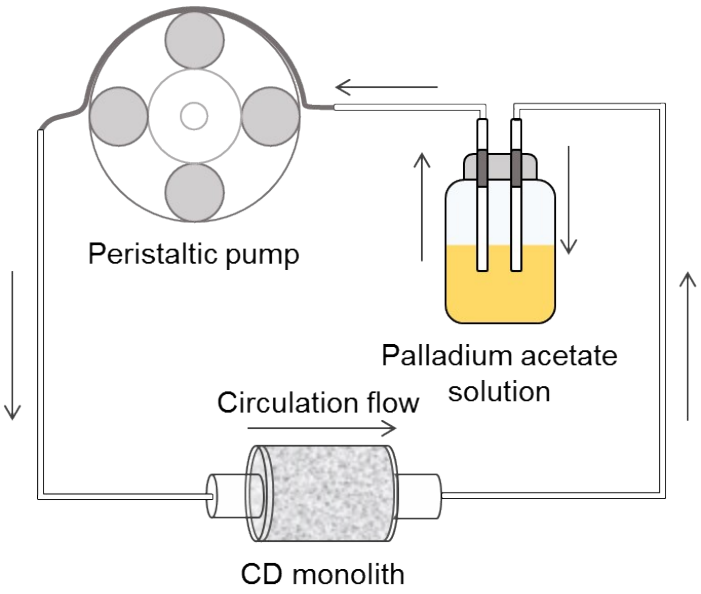

Fig. S1. Circulation flow system for $Pd(OAc)_2$ adsorption by CD monolith.

The peristaltic pump, CD monolith, and $Pd(OAc)_2$ solution were connected as shown in Fig. S1. After adsorption, the eluate was mixed with a $Pd(OAc)_2$ solution. The concentration of $Pd(OAc)_2$ gradually decreased as the amount of adsorption increased. When the flow of the $Pd(OAc)_2$ solution in one direction was completed, the flow direction was reversed.

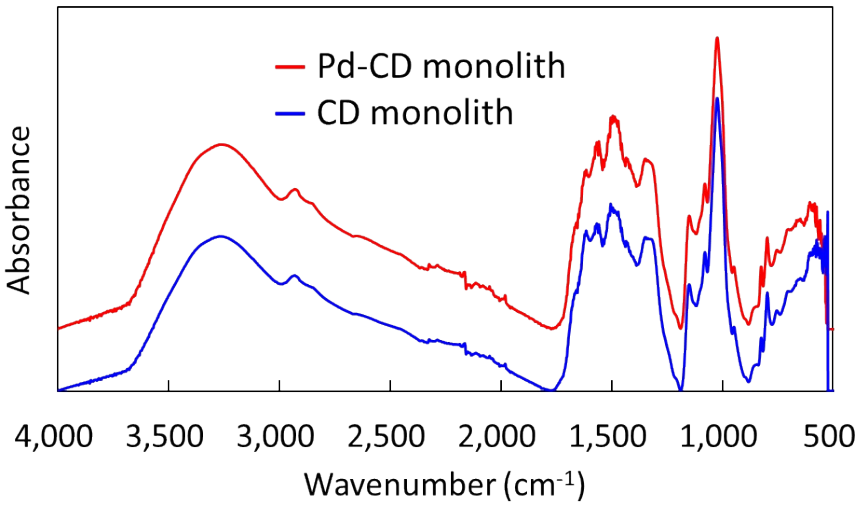

Fig. S2. FT-IR spectra of the Pd-CD monolith (red line) and the CD monolith (blue line).

In the FT-IR spectra, a huge, broad peak at 3300 cm^{-1} was observed and assigned to the –OH group derived from β-cyclodextrin in the Pd-CD monolith. There was no significant change in the spectrum before and after immobilization of the palladium nanoparticles, indicating that the chemical structure did not change.

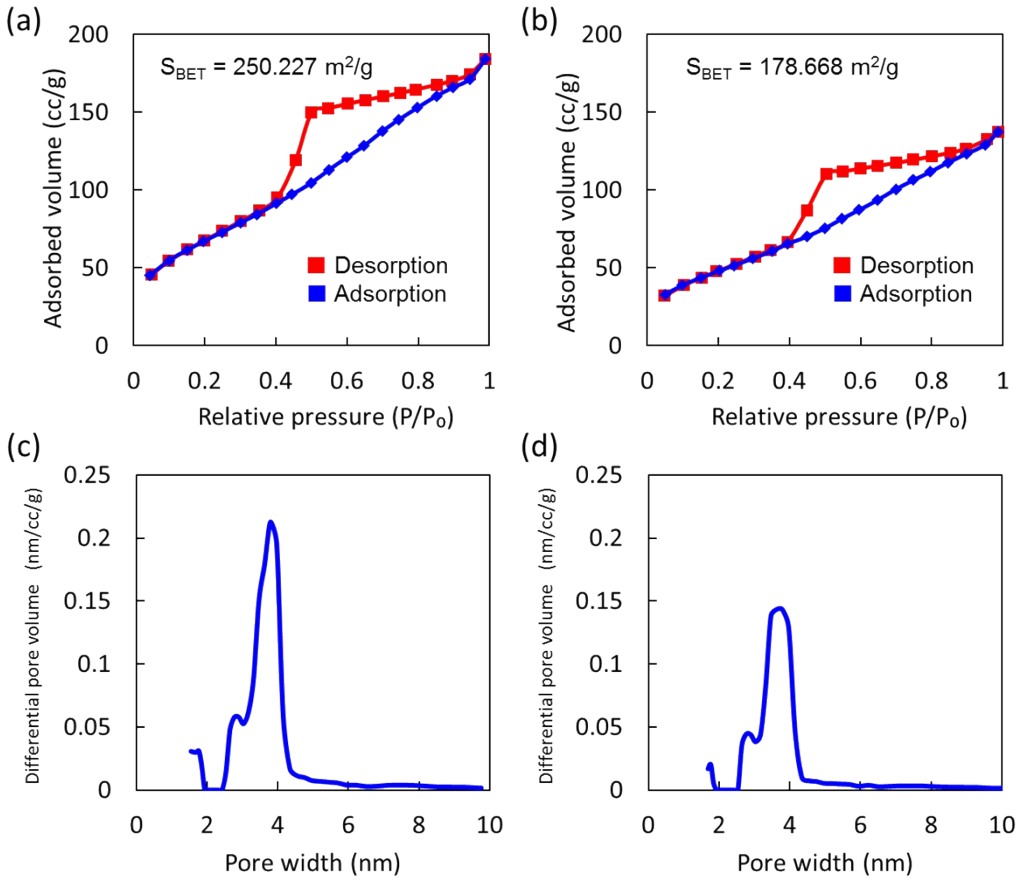

Fig. S3. N_2 gas adsorption/desorption isotherms of **(a)** the CD monolith and **(b)** the Pd-CD monolith. Pore size distributions based on a DFT method of the N_2 gas adsorption isotherm for **(c)** the CD monolith and **(d)** the Pd-CD monolith.

N_2 gas adsorption/desorption isotherms were characterized using a surface area and pore size analyzer (Quantachrome Instruments, NOVA-4200e) to analyze the porous structure. The specific surface area was calculated from the adsorption branch of the isotherm from $P/P_0 = 0.05-0.3$ by the Brunauer-Emmett-Teller (BET) method. The total pore volume was determined from $P/P_0 = 0.95$, and pore size distributions and mesopore sizes were estimated by a non-local density functional theory (NLDFT) method. The adsorption/desorption isotherms of the CD and the Pd-CD monoliths were type Ⅳ of the

IUPAC classification. The specific surface areas of the CD and Pd-CD monoliths were calculated to be 250.227 and 178.668 m^2/g, respectively. The pore size distribution demonstrated that the mesoporous structure of the CD monolith was maintained during the Pd loading process.

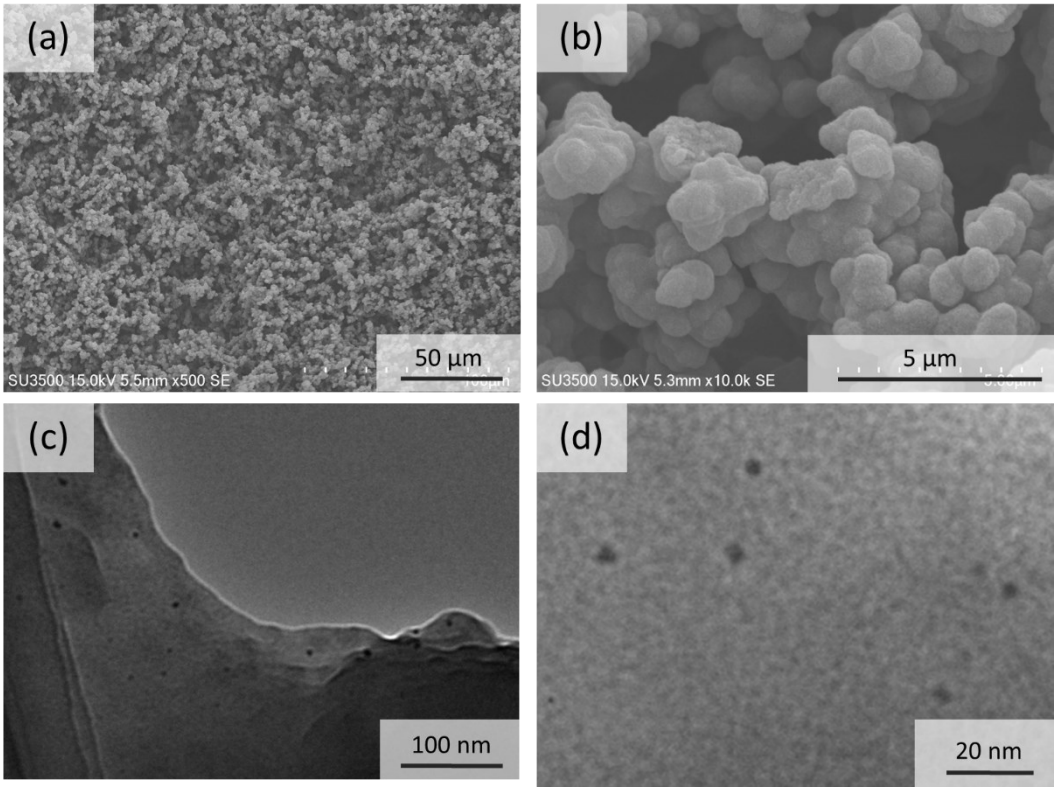

Fig. S4. (a), (b) SEM images and **(c), (d)** TEM images of the Pd-CD monolith.

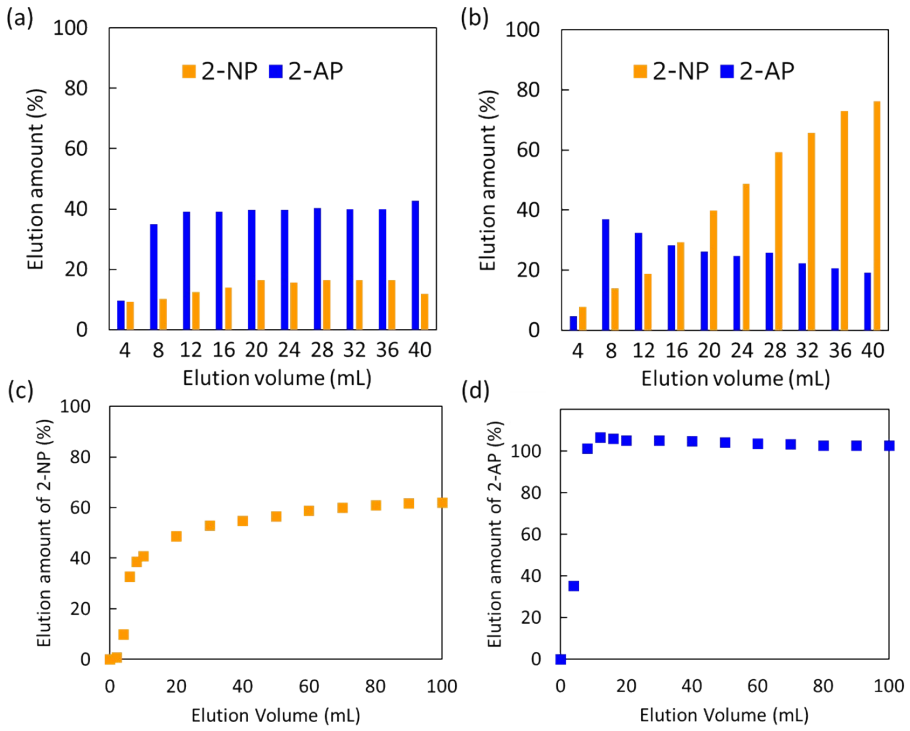

Fig. S5. **(a)** The elution amounts of 2-NP and 2-AP during the 2-NP reduction in the flow system and **(b)** when using Ad-COOH as an inhibitor. Breakthrough curves of **(c)** 2-NP and **(d)** 2-AP adsorption by the Pd-CD monolith.

The reduction of 2-NP, nitrophenol with a lower association constant[2], was conducted in the same manner. In contrast to 4-NP, 2-NP was detected in all eluates and 2-AP production was slightly increased as the reaction progressed (**Fig. S5a**). 2-NP elution was further increased and 2-AP production was reduced in the presence of inhibitors (**Fig. S5b**). The breakthrough curves demonstrated that the Pd-CD monolith has a weak ability to capture 2-NP. The adsorption capacity for 2-AP was slight, as in the case of 4-AP (**Fig. S5c, d**).

Notes and references

1. S. Mizuno, T.-A. Asoh, Y. Takashima, A. Harada and H. Uyama, *Polymer Degradation and Stability*, 2019, **160**, 136–141.

2. T. Kokugan, Kaseno, T. Takada and M. Shimizu, *Journal of Chemical Engineering of Japan*, 1995, **28**, 267–273.