Supporting Information

Chirality-specific hydrolysis of amino acid substrates by cellulose nanofibers

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Experimental details

CNF suspensions were prepared from the appropriate natural sources, according to previous reports.^[1] In brief, pre-treated raw materials were hydrolyzed with aqueous 4 M HCl at 80 °C for 8 h, and the obtained CNFs were suspended in water by a repetitive centrifugation/supernatant-exchange process. The suspensions were stored at 4 °C, and the solvent was exchanged to a buffer solution just before use by a repetitive centrifugation/supernatant-exchange process. For TEM observations, the CNF suspensions were cast onto carbon-coated copper grids, and the images were obtained with a JEOL 2000EX TEM (Jeol) at 200 kV under diffraction contrast in bright-field mode. The substrates were purchased from Biosynthesis. All other reagents were purchased from Nacalai Tesque. Ultrapure water of more than 18.2 M Ω ·cm was supplied by the Milli-Q system (Merck Millipore), and was used throughout all hydrolytic reactions.

For the hydrolysis of the amino acid substrates, 3 μ L (10 mM) of their stock solutions in dimethylsulfoxide was added into 297 μ L of CNF-suspended 10 mM HEPES buffer solution (pH 7.4). The concentrations of the CNFs and substrates were set at 0.5 % (w/v) and 100 μ M, respectively, and the reaction temperature was set at 30 °C. The reaction solutions were then stirred mechanically by a rotator (15 rpm) with double tapping per round. After this incubation, the CNFs were precipitated by centrifugation (15000 rpm, several minutes), and the supernatants were analyzed by ultraviolet-visible light absorption spectroscopy (JASCO V-550 or V-670).



Fig. S1. TEM images of CNFs obtained from (a) tunicate (*Halocynthia*) and (b) green algae (*Cladophora*).



Fig. S2. Analysis of the physical adsorption of arginine and leucine substrates: (a) UV-Vis absorption spectra of the supernatantsafter incubation for 2 h and (b) the amounts remaining in the supernatants determined by their absorbance at 320 nm with (blue) and without (black) CNFs.



Fig. S3. The product amounts for L- (blue) and D-form (light blue) amino acid substrates with CNFs obtained from green algae (*Cladophora*).

References

 [1] (a) J. Araki, M. Wada, S. Kuga, T. Okano, *Colloids Surf. A Physicochem. Eng. Aspects* 1998, 142, 75-82; (b) K. Igarashi, M. Wada, R. Hori, M. Samejima, *FEBS J.* 2006, 273, 2869-2878.