Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Topochemical synthesis and catalysis of metal nanoparticles exposed on crystalline cellulose nanofibers

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Experimental details

Preparation of CSNFs.[1] Never-dried cellulose (tunicate, *Halocynthia aurantium*, 2.0 g of cellulose content) was suspended in distilled water (150 mL) containing TEMPO (0.025 g) and NaBr (0.25 g). TEMPO-mediated oxidation of the cellulose slurry was started by adding 13% NaClO aq. (NaClO: 1.8 mmol g-cellulose^{-1}) and conducted at room temperature under gentle agitation. The pH (which otherwise decreases as the reaction proceeds) was maintained at 10.5 by adding 0.5 M NaOH. When the pH change ceased we concluded that the reaction was finished, and adjusted the pH to 7.0 by adding 0.5 M HCl. The TEMPO-oxidized product was thoroughly washed with distilled water by filtration, followed by sonication for a few seconds.

Preparation of AuNPs@CSNFs, AuNPs@Cel and Cel-free AuNPs. An aqueous solution of $HAuCl_4$ (0.3 mM, 2 mL) was added to an aqueous suspension of CSNFs (0.16 wt%, 2 mL), and the mixture was stirred at 277 K for 3 min. An aqueous solution of $NaBH_4$ (6 mM, 2 mL) was then added over a period of 1 min, and the mixture was stirred at 277 K for 2 h. AuNPs@Cel and Cel-free AuNPs were prepared with and without untreated native cellulose, respectively, instead of CSNFs.

Preparation of AgNPs@CSNFs. An aqueous solution of $AgNO_3$ (0.3 mM, 2 mL) was added to a CSNFs/water suspension (0.16 wt%, 2 mL) and the mixture was stirred at 277 K for 3 min. Then an aqueous solution of $NaBH_4$ (6 mM, 2 mL) was added over 1 min, followed by additional stirring at 277 K for 2 h.

Preparation of AuNPs@CSNFs-containing paper. AuNPs@CSNFs-containing paper was prepared by incorporating CSNFs into a paper composite, followed by *in situ* synthesis of AuNPs onto the embedded CSNFs. CSNFs-containing paper was prepared by a simple papermaking process. A water suspension of pulp fibers (0.135 wt%, 10 mL) was mixed with an aqueous solution of poly(amideamine)-epichlorohydrin resins (0.125 wt%, 216 μL) as a wet-strengthening agent, and stirred for 3 min. The mixture was added to a CSNFs/water suspension (0.05 wt%, 0.5 mL), followed by stirring for 3 min and dewatering on a polytetrafluoroethylene membrane filter. The resulting wet-state paper was dried at 378 K for 1 h. Subsequently, as-prepared CSNFs-containing paper was immersed in an aqueous solution of $HAuCl_4$ (0.04 mM, 5 mL) at room temperature for 20 h, followed by washing with deionized water and reduction with an aqueous solution of $NaBH_4$.

Analyses. UV-Vis absorption spectra were recorded at room temperature using a U-3000 spectrophotometer (Hitachi, Ltd., Japan). TEM and SAED analyses were performed using a JEM1010 instrument (JEOL, Ltd., Japan). XRD measurements were carried out with an XD-D1 X-ray diffractometer (Shimadzu, Ltd., Japan) with Ni-filtered Cu$K\alpha$ radiation (λ=1.5418 Å). AFM observation was performed under ambient conditions using a NanoScope IIIa atomic force microscope (Veeco Instruments, Inc., USA) in tapping mode.

Catalytic performance test. Aqueous 4-NP solution (0.05 mM, 30 mL) was mixed with $NaBH_4$ (1.5 mmol), and an aqueous dispersion of AuNPs@CSNFs (100 μL, Au content 1.0×10^{-2} μmol) was added. Reaction was carried out at 298 K with continuous stirring. At appropriate time intervals, an aliquot of reaction mixture (1.0 mL) was filtered through a 0.2 μm membrane filter, and the UV-Vis absorption spectrum of the sample was recorded at room temperature. According to a previous report,[2] the rate constant for the reduction process was determined by measuring the change in absorbance at 400 nm as a function of time.

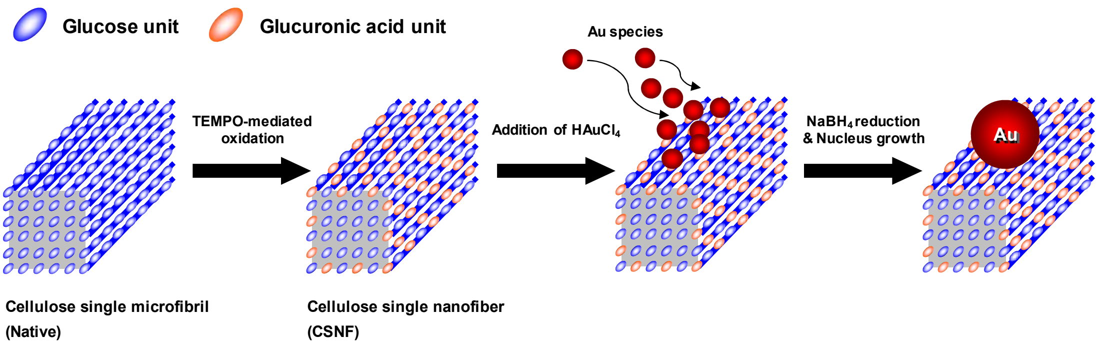

Fig. S1 Schematic diagram of the topochemical synthesis of AuNPs on crystalline CSNFs.

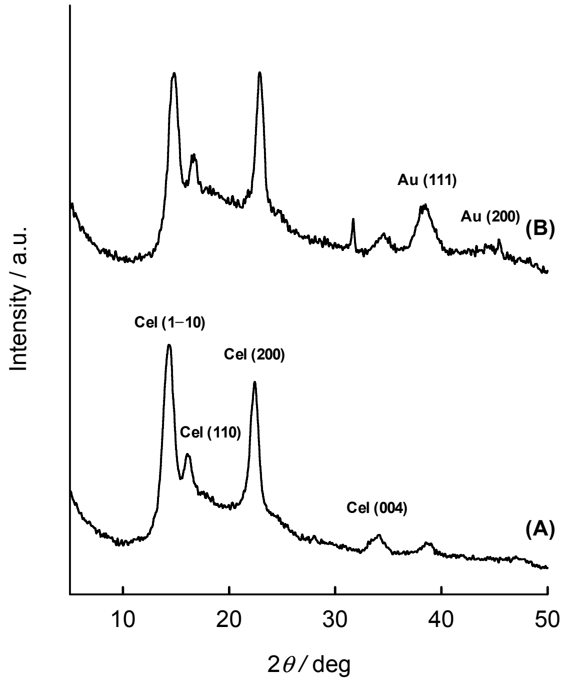

Fig. S2 XRD patterns. (A), CSNF. (B), AuNPs@CSNF. The CSNFs maintained the crystalline structure of native cellulose (cellulose I) after AuNPs synthesis.

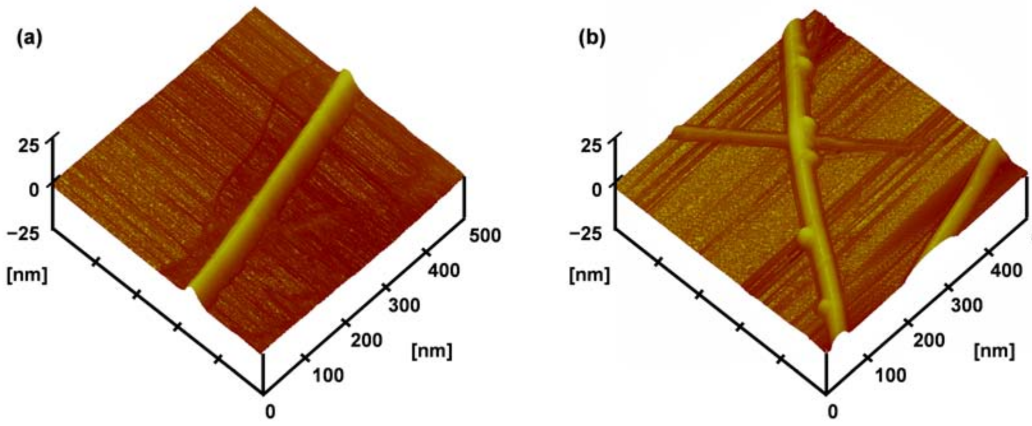

Fig. S3 AFM images. (a), CSNF. (b), AuNPs@CSNF. The AFM image of AuNPs@CSNFs revealed that AuNPs were exposed on the surfaces of CSNFs.

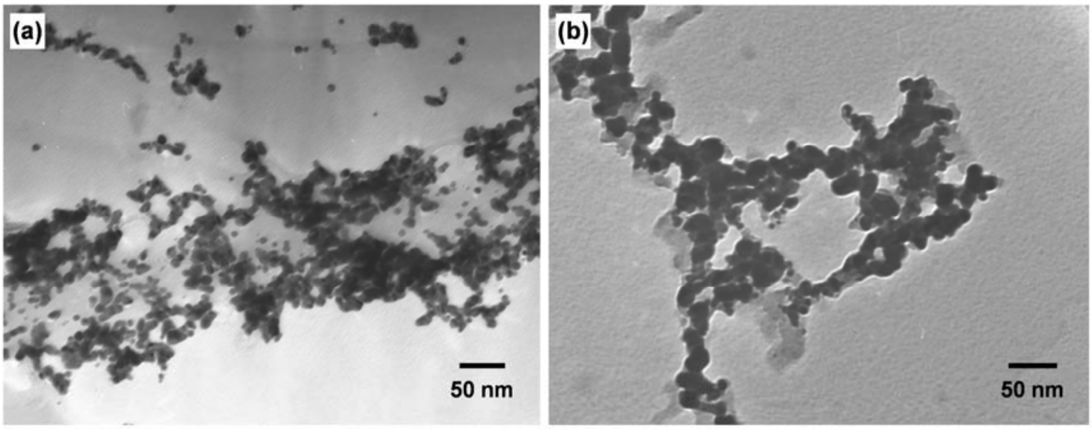

Fig. S4 TEM images. (a), AuNPs@Cel. (b), Cel-free AuNPs. In both cases, large aggregates of as-synthesized AuNPs were observed.

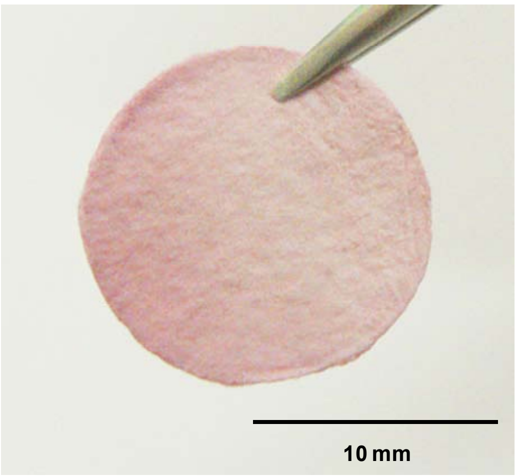

Fig. S5 Optical image of AuNPs@CSNFs-containing paper. The pink color of this paper was derived from surface plasmon resonance of AuNPs topochemically-synthesized on the CSNFs in the paper matrix. The AuNPs@CSNFs-containing paper gave a turnover frequency of 34.6 in the 4-NP reduction process, and could be easily recycled without catalytic deactivation during multiple cycle testing.

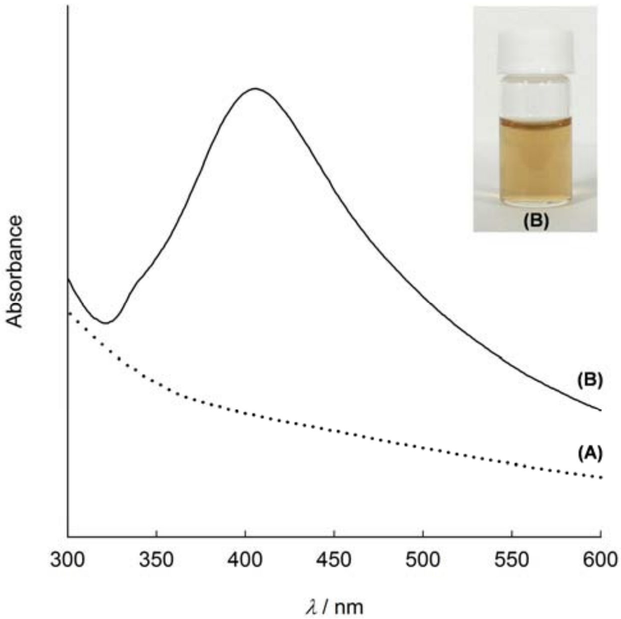

Fig. S6 UV-Vis absorption spectra. (A), an aqueous suspension of CSNFs. (B), an aqueous suspension of AgNPs@CSNFs. The surface plasmon resonance band at *ca.* 400 nm confirmed the formation of AgNPs.[3]

References

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[2] K. Kuroda, T. Ishida and M. Haruta, *J. Mol. Catal. A*, 2009, **298**, 7.

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