

Electronic supplementary information

Cellulose-based catalytic membranes fabricated by deposition of gold nanoparticles on natural cellulose nanofibres

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Experimental details

Materials

The filter paper used in this work were commercial quantitative one. Titanium *n*-butoxide [Ti(O^{*n*}Bu)₄], poly(diallyldimethylammonium chloride) (PDDA, M_w = 2000,000 ~ 350,000) and poly(sodium-*p*-styrenesulfonate) (PSS, M_w = 70,000) were purchased from Sigma-Aldrich; potassium tetrachloroaurate (III) (KAuCl₄), 4-nitrophenol (4-NP) and sodium borohydride (NaBH₄) were bought from J&K Co. All the other chemicals were of AR grade and used as received. All aqueous solutions were prepared using Milli-Q water (resistivity, 18.2 MΩ cm).

Surface modification of filter paper with titania nanocoating

A piece of ordinary commercial filter paper (~2 cm in diameter) was put in a suction filtering unit, washed with ethanol by suction filtration and then dried in flowing air. A solution of Ti(O^{*n*}Bu)₄ in 1:1/*v*:*v* toluene/ethanol (100 mM, 10 mL) was added into the funnel, the first 5 mL of solution was slowly filtered through the filter paper, the remaining portion was allowed to stand for 3 min to realize chemisorption of titanium *n*-butoxide, and then suction-filtered slowly. Subsequently, adequate ethanol was immediately passed through the filter paper *via* suction to wash away any residual metal alkoxide, followed by passing through 20 mL of pure water within 3 min to promote hydrolysis of titanium alkoxide and condensation of the resultant titania gel layer. At last, the filter paper was washed with copious ethanol and intensively dried with air flow, thus finishing a deposition cycle. By repeating the surface sol-gel process for five cycles, each cellulose nanofibre of filter paper was coated with a uniform titania gel film, and the resultant cellulose/titania composite paper

was denoted as cellulose/(TiO₂)₅.

Introduction of Au-NP catalyst on titania gel film pre-coated filter paper

To fabricate the cellulose-based catalytic membranes, a piece of the as-prepared cellulose/(TiO₂)₅ paper was put in a suction filtering unit and kept in dark. Then, an aqueous solution of PDDA (1 mg/mL, 6 mL) was added into the funnel, the first 3 mL of which was slowly filtered through the titania-coated filter paper, and the rest of which was allowed to stand for 15 min to ensure the assembly of PDDA layer on the titania gel pre-coating layer, and then suction-filtered slowly, followed by washing with abundant water. Subsequently, an aqueous solution (6 mL) containing PSS (1 mg/mL) and KAuCl₄ (10 mM) was added into the funnel, the first 3 mL of which was slowly suction-filtered, and the rest of which was allowed to stand for 15 min to ensure the assembly of the two-component layer comprised of PSS and KAuCl₄ (denoted as PSS•KAuCl₄), and then suction-filtered slowly, followed by washing with abundant water. By repeating the PDDA/PSS•KAuCl₄ bilayer deposition process for *n* times, a uniform titania/PDDA/PSS/KAuCl₄ composite film was deposited on each cellulose nanofibre of filter paper. Afterwards, a solution of NaBH₄ in 1:1/v:v water/ethanol (100 mM, 20 mL) was added into the funnel, the first 10 mL of which was slowly filtered through the composite paper, and the rest of which was allowed to stand for 30 min to ensure the sufficient reduction of the assemble KAuCl₄ to gold nanoparticles, and then suction-filtered slowly, followed by washing with abundant ethanol and drying in air flow. As such, cellulose-based catalytic membranes were obtained, which were denoted as cellulose/(TiO₂)₅/Au@(PDDA/PSS)_n.

Catalytic reactions

The catalytic activities of the cellulose-based catalytic membranes were tested by a facile filtration process, which is described as follows. A piece of the cellulose-based catalytic membrane (*i.e.*, the cellulose/(TiO₂)₅/Au@(PDDA/PSS)_n paper, *n* = 10 or 20) was put in a suction filtering unit, then 10 mL aqueous feed solution of the reaction mixture containing 4-NP (0.1 mM) and NaBH₄ (10 mM) was added into the funnel, letting it drip naturally. Meanwhile, the filtrate was totally collected in a clean vessel, which was subjected to the measurement of UV-vis spectrum. Afterwards, the collected filtrate underwent the same filtration process for the second or third time, and the UV-vis spectrum of the corresponding

filtrate was also measured. The catalytic efficiency of the cellulose-based catalytic membranes were evaluated in terms of the conversion of 4-NP.

Determination of the Au content

5 mg of the cellulose-based catalytic membrane (*i.e.*, the cellulose/(TiO₂)₅/Au@(PDDA/PSS)_n paper) was cut into pieces and dispersed in 2 mL of aqua regia, and the resultant suspension was vigorously stirred for 1 h, followed by centrifugation. Then, 1 mL of the supernatant was diluted with Milli-Q water to 10 mL, which was subjected to inductively coupled plasma mass spectrometry (ICP-MS) to determine the concentration of gold element. The Au contents in the cellulose-based catalytic membranes were calculated according to the concentrations of gold element and the weight of the corresponding samples.

Characterizations

UV-vis spectra were measured on a Shimadzu UV-2450 spectrophotometer in the diffuse reflectance mode for cellulose-based samples employing an integrating sphere accessory with pure filter paper as reference, or in the transmission mode for solution-based samples with pure water as reference. Specimens for scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations were prepared by dispersing the cellulose-based samples in the mixed solvent of 1:1/v:v water/ethanol, followed by dropping the suspension on silicon wafer for SEM examination or on carbon-coated copper mesh grid for TEM inspection. Moreover, all specimens used for FE-SEM observations were sputtered with platinum nanoparticle coating to increase their conductivity, and the FE-SEM examinations were performed on a Zeiss ULTRA 55 instrument at an acceleration voltage of 3 kV; TEM observations were carried out on a Hitachi HT-7700 instrument at an acceleration voltage of 100 kV.

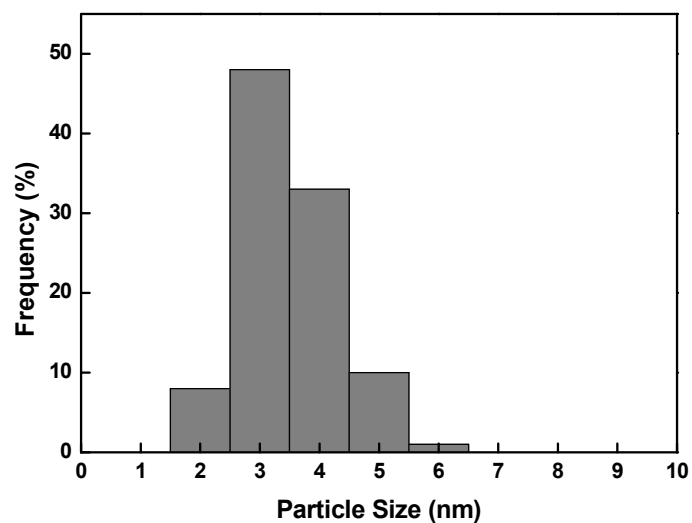


Fig. S1 Histogram of gold nanoparticle size distribution of sample cellulose/(TiO₂)₅/Au@(PDDA/PSS)₁₀ paper.

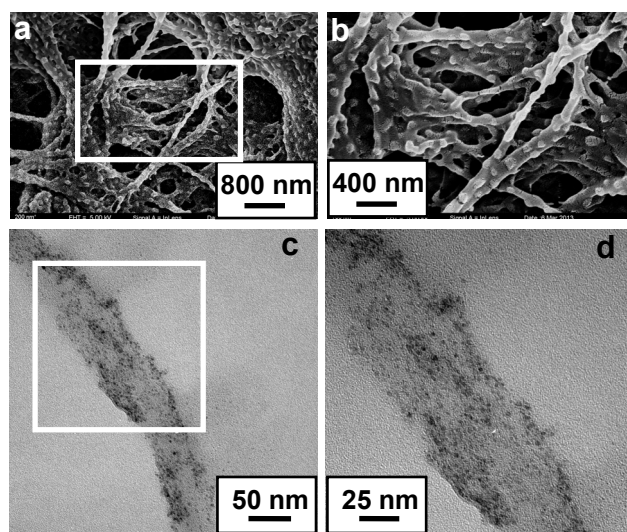


Fig. S2 (a) FE-SEM image of the cellulose/(TiO₂)₅/Au@(PDDA/PSS)₂₀ paper. (b) FE-SEM image of the morphological details of the boxed area in (a). (c) TEM image of the cellulose/(TiO₂)₅/Au@(PDDA/PSS)₂₀ paper. (d) TEM image of the morphological details of the boxed area in (c)

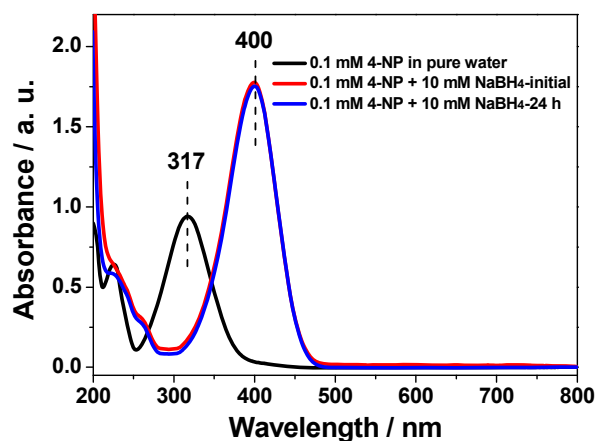


Fig. S3 UV-vis spectra of aqueous solution of 4-NP (0.1 mM, black curve), aqueous solution of the mixture containing 4-NP (0.1 mM) and NaBH₄ (10 mM), which was freshly prepared (red curve), as well as aqueous solution of the mixture containing 4-NP (0.1 mM) and NaBH₄ (10 mM), which was set for 24 h (blue curve).

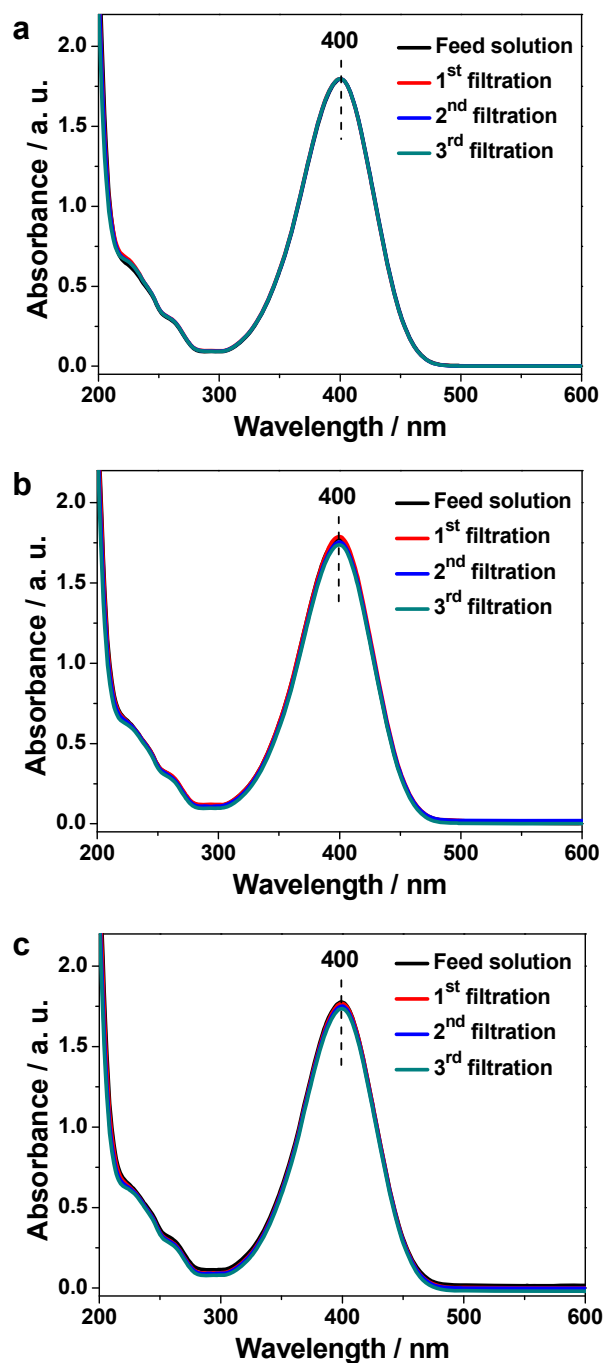


Fig. S4 UV-vis spectra of the initial aqueous feed solution containing 4-NP and NaBH₄ (black curve) as well as the spectra of the filtrate after filtering the feed solution through (a) the cellulose/(TiO₂)₅/(PDDA/PSS)₁₀ paper and (b) the cellulose/(TiO₂)₅ paper and (c) pure filter paper for single (red curve), double (blue curve) and triple (green curve) cycles.