

Supporting Information

Noncloggingly Sieving Sub-6-nm Nanoparticles of Noble Metals into Conductive Mesoporous Foams with Biological Nanofibrils

Zengbin Wang,^{1,2} Jie Xu,¹ Penggang Wang,¹ Yue Zhang,² Jun You,^{1,3} and Chaoxu Li^{1,*}*

¹CAS Key Lab of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Songling Road 189, Qingdao 266101, P. R. China.

²Institute of Material Science and Engineering, Ocean University of China, Qingdao, Shandong, 266100 P.R. China.

³Ministry-of-Education Key Laboratory for the Green Preparation and Application of Functional Materials, School of Materials Science and Engineering, Hubei University, Wuhan, 30062, PR China.

*Corresponding author: C. Li (Email: licx@qibebt.ac.cn); J. You (Email: youjun@qibebt.ac.cn)

Fabrication of biological nanofibrils. The shells of *Portunid* crabs were peeled off and washed with abundant deionized water after steaming for 15 min. Subsequently, they were immersed in 2M HCl for 48 h and then 4 wt% NaOH for 48 h, followed by washing with abundant water to remove minerals and proteins. Finally, purified chitin was obtained after bleaching treatment in 0.3% NaClO₂ at 80 °C for 3.5 h. In order to directly exfoliate chitin nanofibrils without chemical erosion, the purified chitin (2g) was immersed in DMSO solution (500 mL) containing 3 mg/mL KOH and then vigorously stirred at room temperature for 1 week. After centrifugally washing with water (pH~8.5), the product was exposed to ultrasonication (BILON92-II, Shanghai, China) with the power of 300 W for 9 min. The transparent well-dispersed chitin nanofibrils suspensions were obtained after centrifugation (CENCE H1850, Hunan, China) at 9000 rpm for 30 min to remove the un-exfoliated aggregates.

In order to obtain the deacetylated chitin nanofibrils, purified chitin (5 g) were deacetylated in 33 wt% NaOH (125 mL) containing 0.15 g NaBH₄ by vigorously stirring at 90 °C for 4 h. Subsequently, the partially deacetylated chitin were washed with deionized water and further dispersed in acetic acid aqueous solution (pH 3.5). After 1-week mechanical agitation, the suspension was exposed to ultrasonication with the power of 400 W for 30 min. The deacetylated chitin nanofibrils suspensions were obtained after centrifugation at 9000 rpm for 30 min to remove the un-exfoliated aggregates.

In order to fabricate TEMPO-oxidized cellulose nanofibrils, dry kraft pulp (5 g) was subjected to oxidation in a mixed solution (500 mL) of TEMPO (0.08 g), NaClO (80 mmol) and NaBr (0.5 g) under alkaline conditions (pH = 10.5) for 7 h with vigorous stirring. After washing with deionized water for 3 times, the resultant products were mechanically homogenized with 3 passes at 50 MPa and pH ~7.0 in a pressure micro-fluidizer (MRT model CR5). The viscous product (0.18 wt%) was then centrifuged at 9000 rpm to remove un-exfoliated aggregates and stored at 4 °C for characterization.

Silk nanofibrils were regenerated from silk fibroin. Typically, *Bombyx mori* cocoon was degummed twice in the boiling solution of 0.5 wt % NaHCO₃ for 30 min. After thoroughly washing in deionized water, the dried purified silk was dissolved in the aqueous solution of LiBr (9.3 M) at 60 °C for 1 h under continuously stirring. Subsequently, the viscous silk solution (10 wt%) was dialyzed with deionized water at 4 °C for nearly 1 week. Finally, silk nanofibrils were obtained after centrifugation at 8000 rpm for 30 min to remove the aggregates.

Synthesis of Platinum nanoparticles. Pt nanoparticles were prepared according to the literature.^{S1} Typically, 0.8 mL H₂PtCl₆•6 H₂O (34.4 mM) was dissolved in 88 mL deionized water to give a precursor solution with a metal content of 0.14 mmol. After stirring for about 1 min, 2 mL of sodium citrate solution (1 wt %) were introduced, followed by adding ice-cold reducing agent solution (10 mL water contained 5 mg of NaBH₄ and 13.5 mg of sodium citrate). After 1 h reaction, Pt nanoparticles were obtained and stored at less than 4 °C in a refrigerator.

Calculation of porosity of mesoporous foams. The porosity (P) of mesoporous foams was calculated by $P=1-\rho/\rho_c$, where ρ and ρ_c are the density of mesoporous gold foams (2.07 g/cm³) and bulk gold (19.32 g/cm³) respectively. The density of mesoporous gold foams was determined by weighting the samples and testing its volumes. A porosity of 90% indicated that the materials possessed abundant pores.

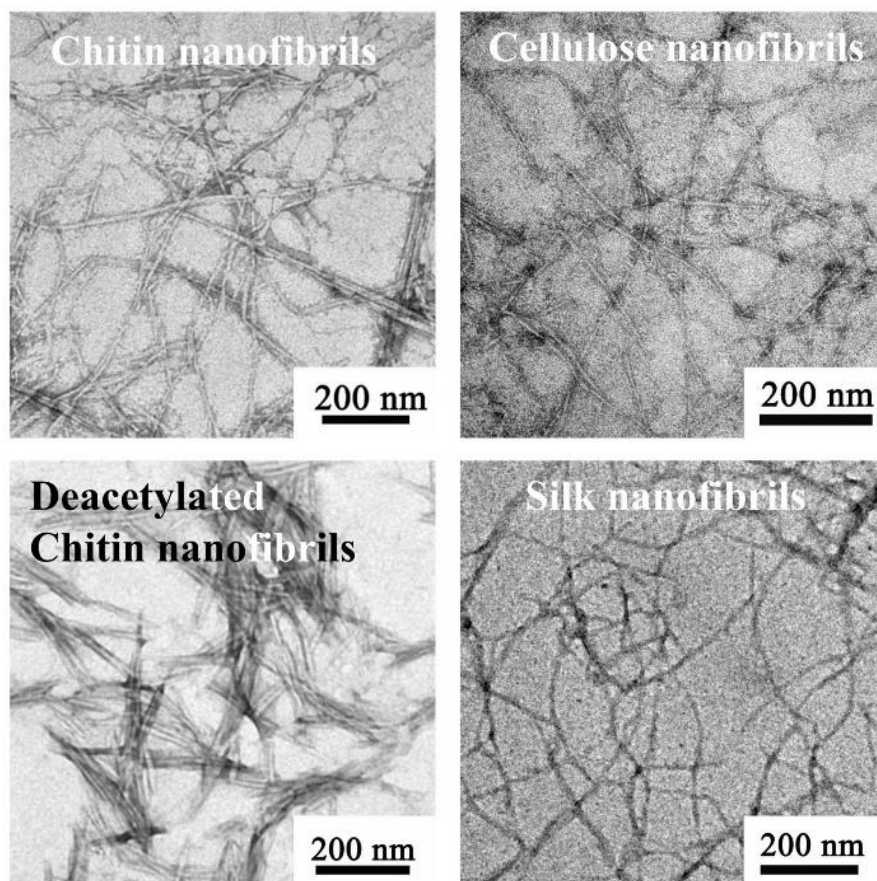


Figure S1. TEM images of biological nanofibrils.

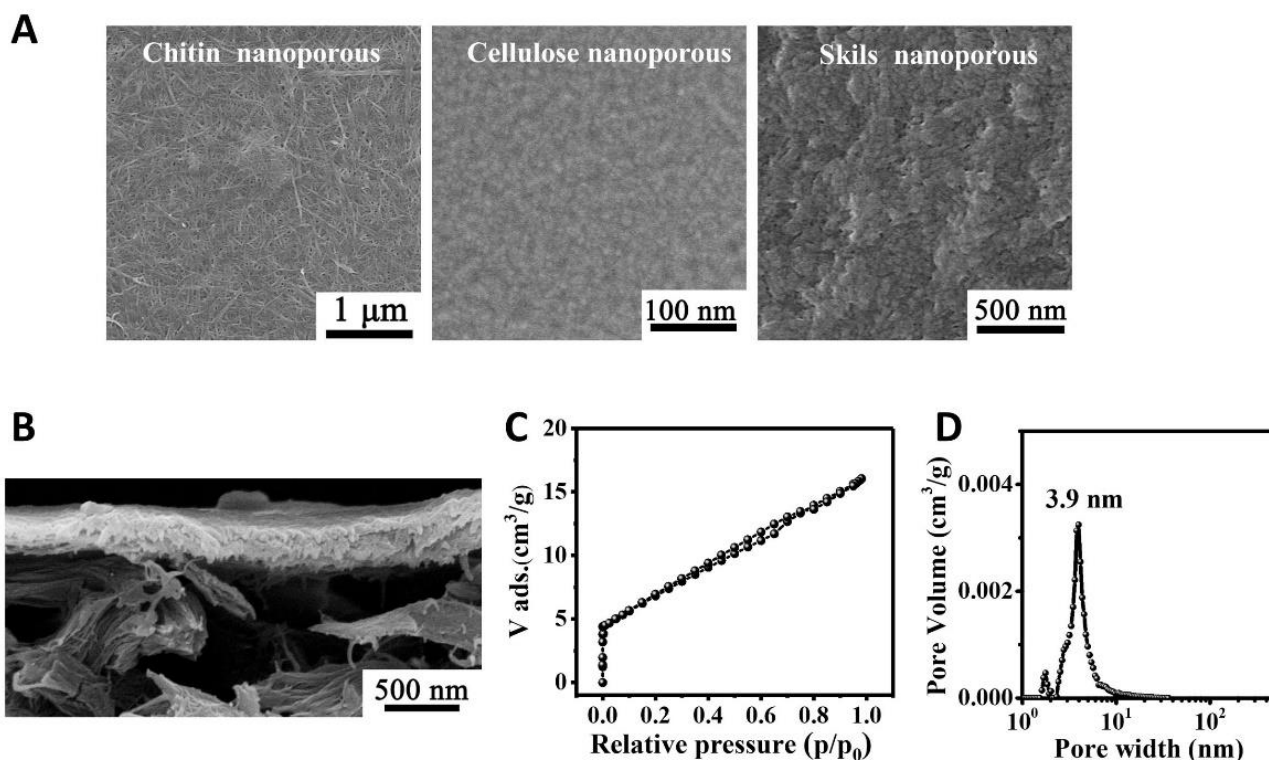


Figure S2. (A) Surface SEM image of biological nanofibrils membranes. (B) Cross-sectional SEM image of chitin nanofibrils membranes. N₂ adsorption-desorption curve (C) and DFT fitted pore size distribution (D) of air-dried chitin nanofibrils membranes.

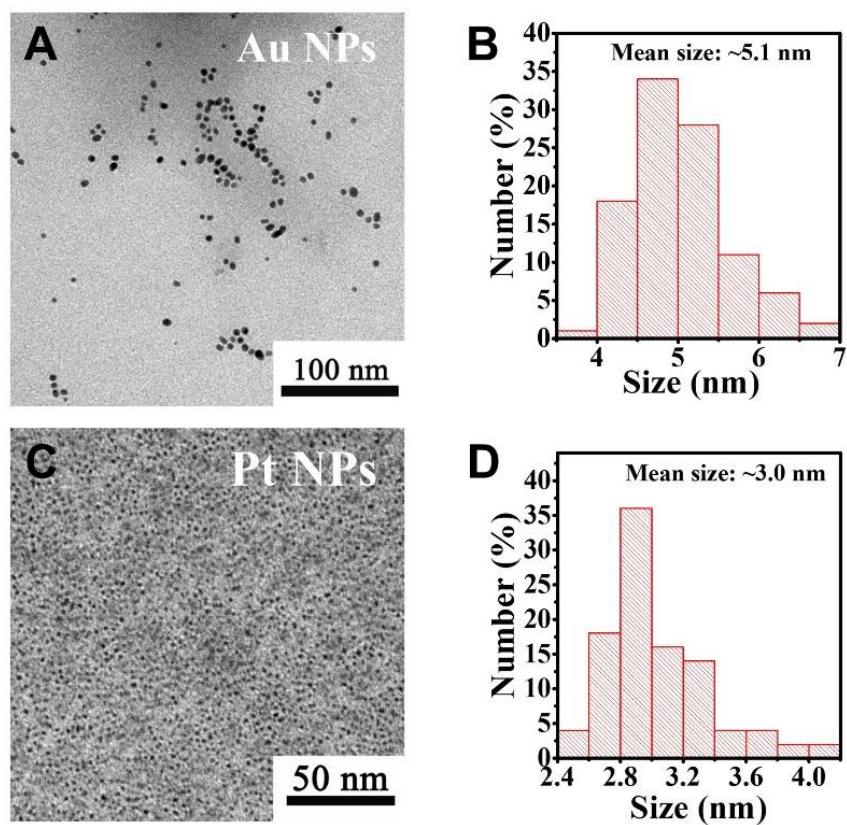


Figure S3. TEM images and corresponding particle size histograms of Au NPs (A&B) and Pt NPs (C&D).

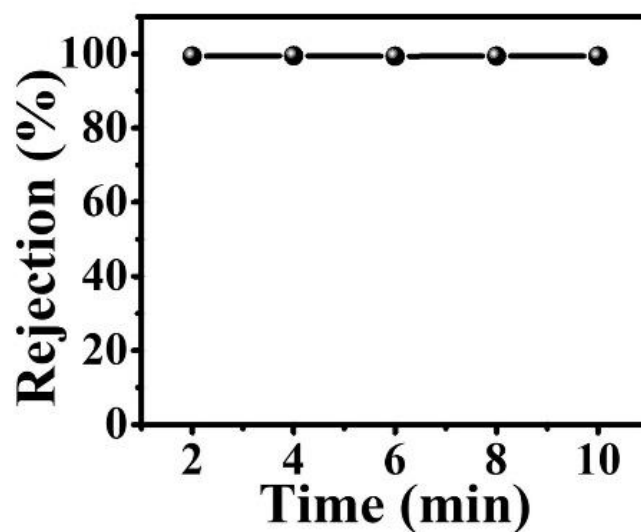


Figure S4. Time dependence of rejection of Au nanoparticles. Thickness of nanoporous layer: 220 nm.

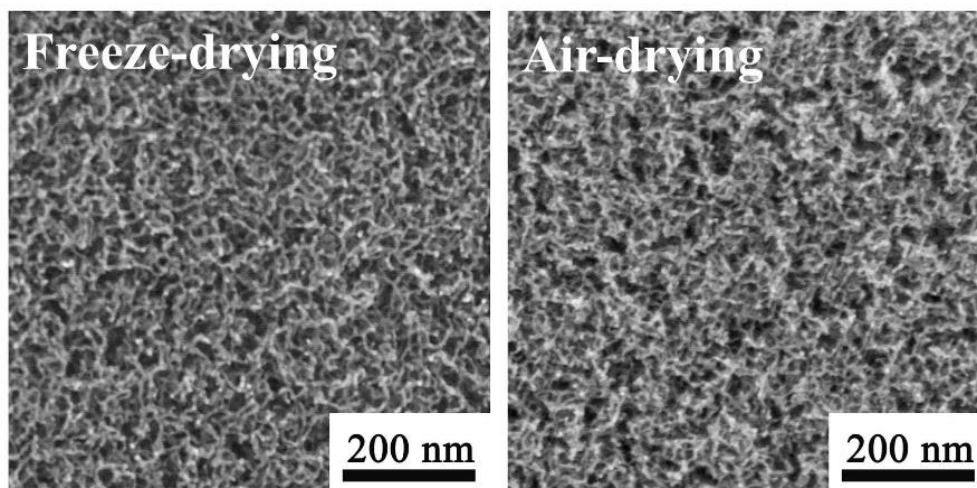


Figure S5. Surface SEM images of mesoporous Au foams prepared by different drying procedures.

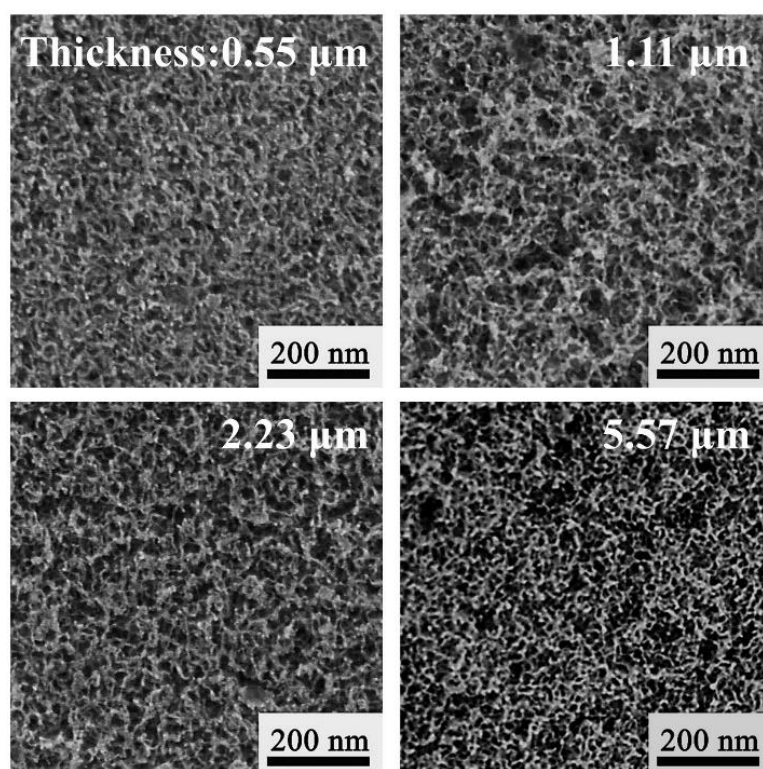


Figure S6. Surface SEM images of mesoporous Au foams with different thickness.

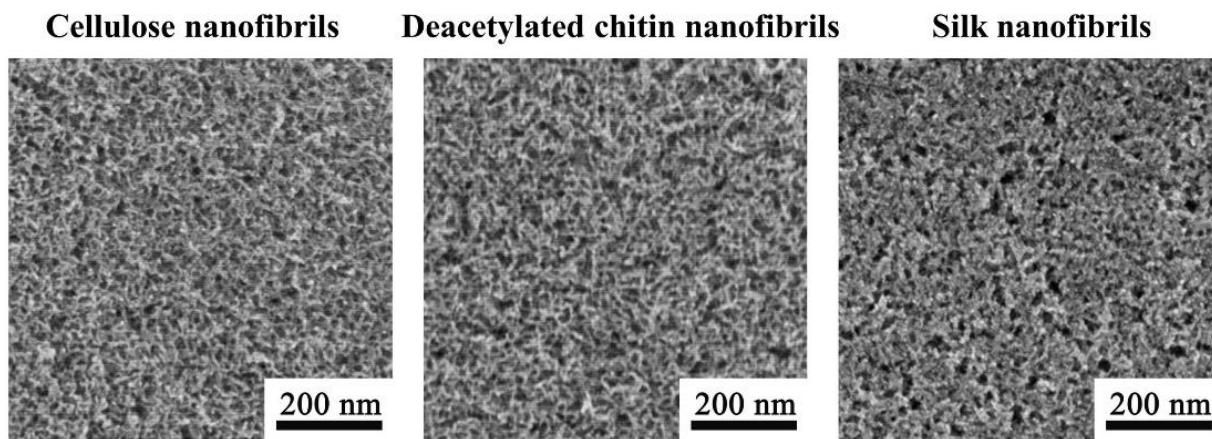


Figure S7. Surface SEM images of mesoporous Au foams prepared by using TEMPO-oxidized cellulose nanofibrils, deacetylated chitin nanofibrils and silk nanofibrils.

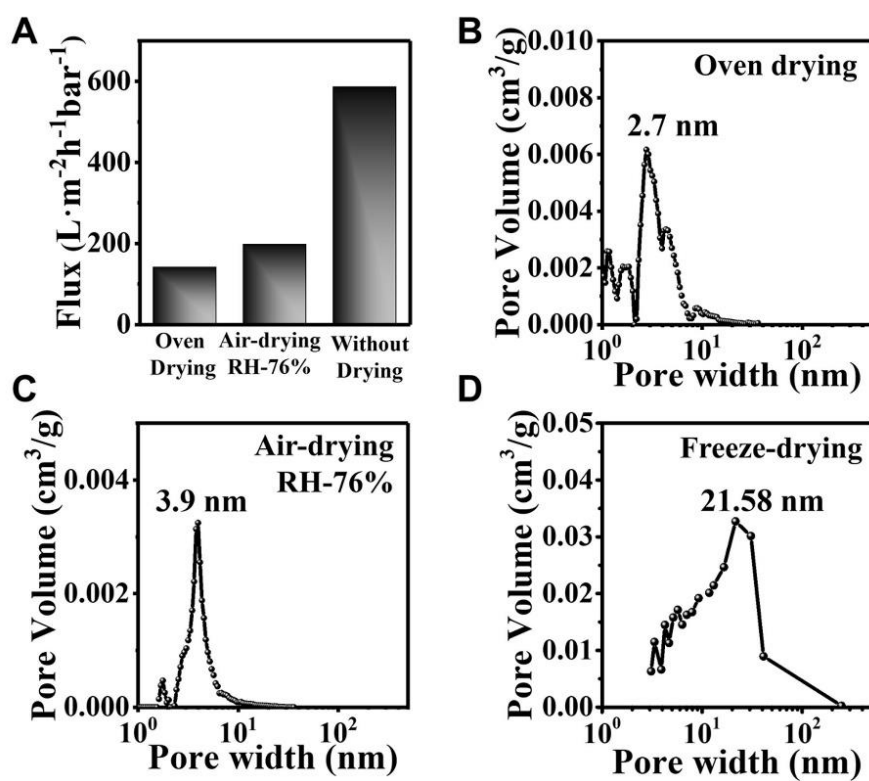


Figure S8. (A) Water flux of layer of chitin nanofibrils with different pore size. (B-D) Pore size distribution of nanoporous layer prepared by different drying procedures.

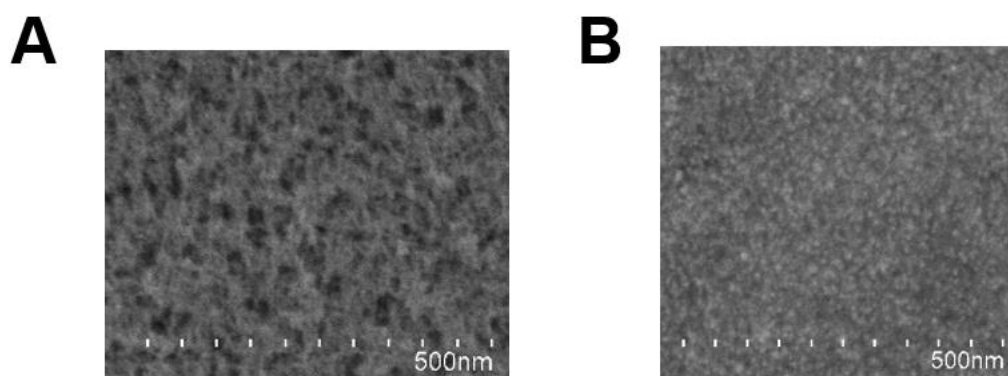


Figure S9. Surface SEM images of mesoporous Au foams prepared by using layers of chitin nanofibrils with pore size of 2.7 nm (A) and 21.58 nm (B).

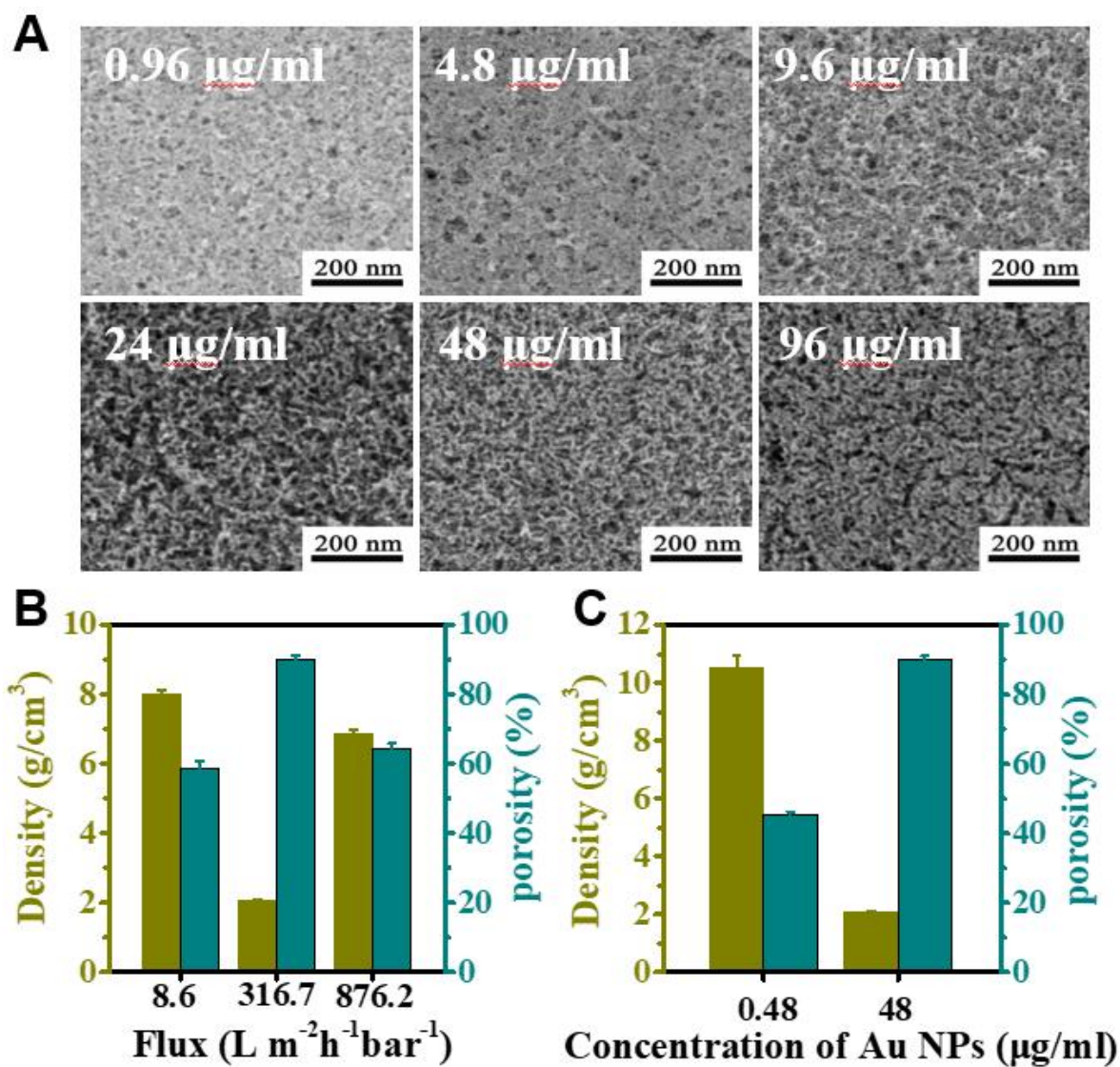


Figure S10. Surface SEM images of mesoporous Au foams prepared by filtering Au NPs suspensions with different concentrations. The density and porosity of mesoporous foams prepared with different flux (C) and concentration of Au NPs (D).

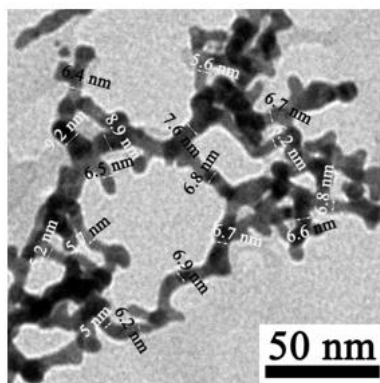


Figure S11. TEM image of Au network with indicated diameters.

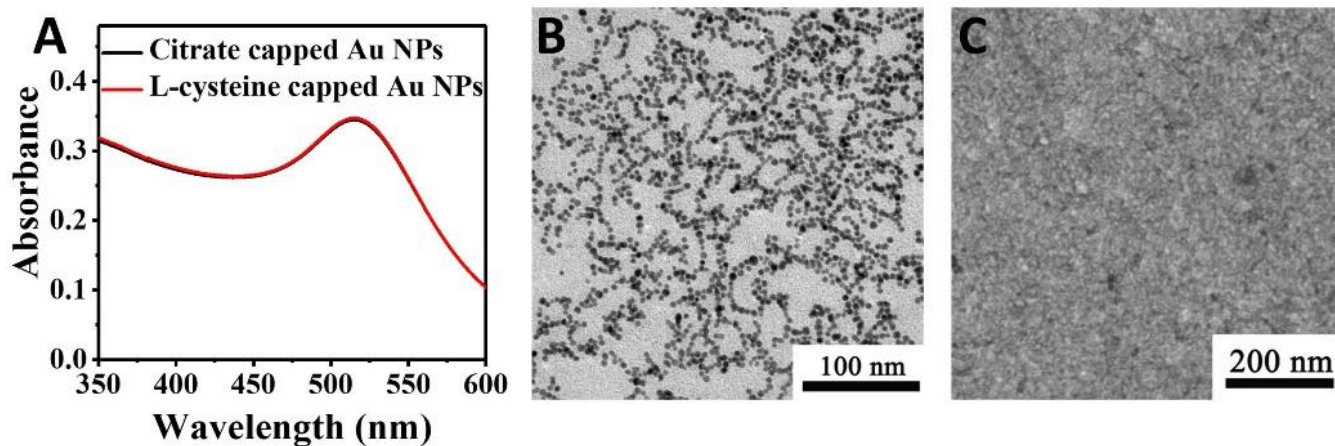


Figure S12. (A) UV-Vis absorption of Au NPs capped with different ligands. (B) TEM images of L-cysteine capped Au NPs. (C) Surface SEM images of mesoporous Au foams prepared by filtering L-cysteine capped Au NPs suspension. Layer thickness of chitin nanofibrils: 220 nm; Concentration of Au NPs: 48 $\mu\text{g/mL}$; Applied pressure: 0.95 bar.

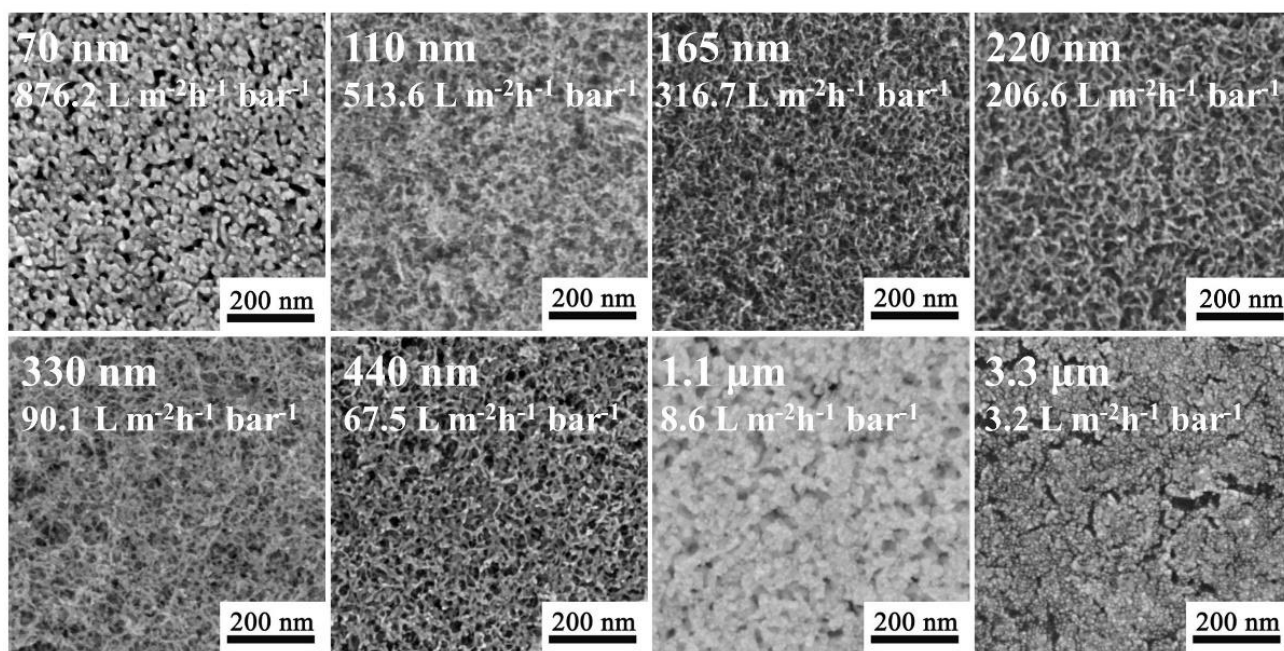


Figure S13. Effect of layer thickness of chitin nanofibrils on morphologies of mesoporous Au foams.

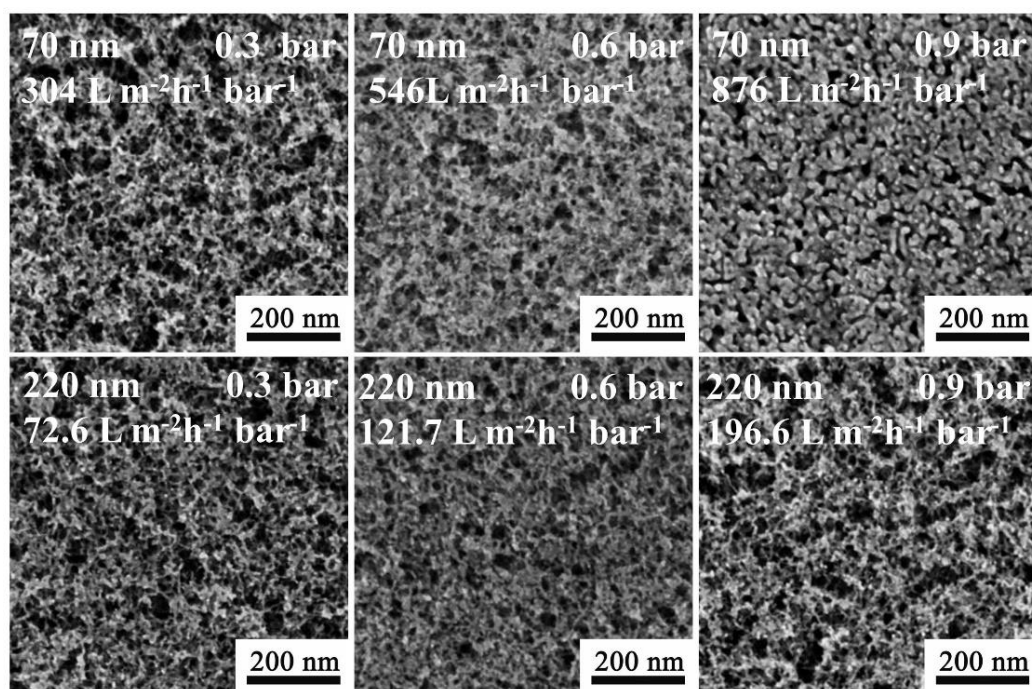


Figure S14. Effect of filtration pressure on morphologies of mesoporous Au foams.

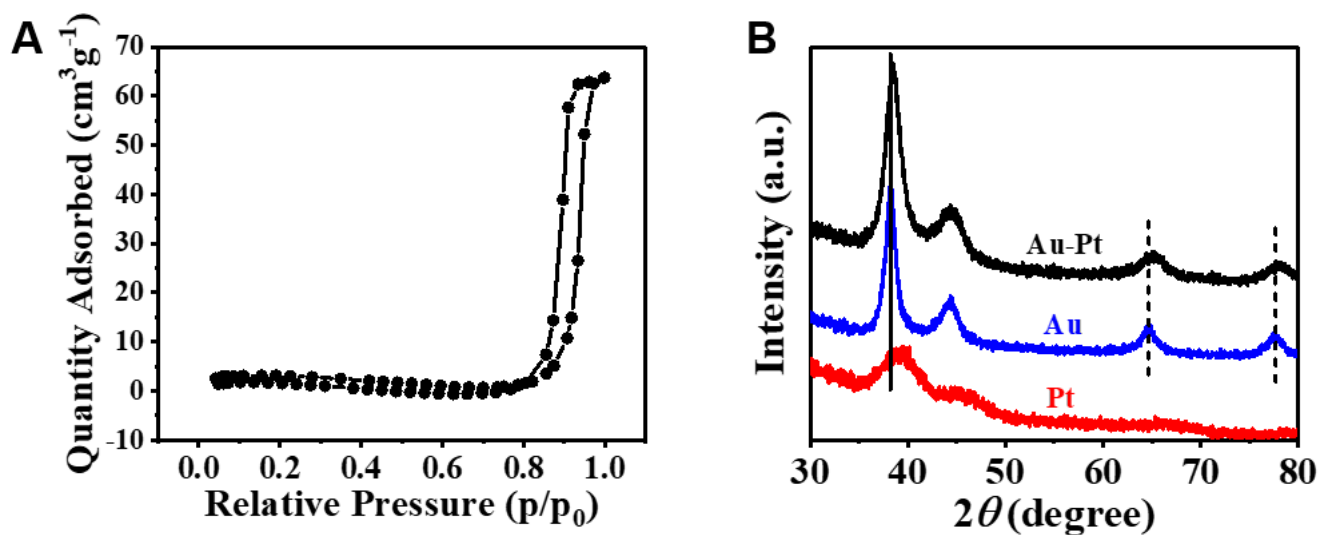


Figure S15. (A) N_2 adsorption-desorption curve of mesoporous Au foams. (B) XRD patterns of various mesoporous metallic foams.

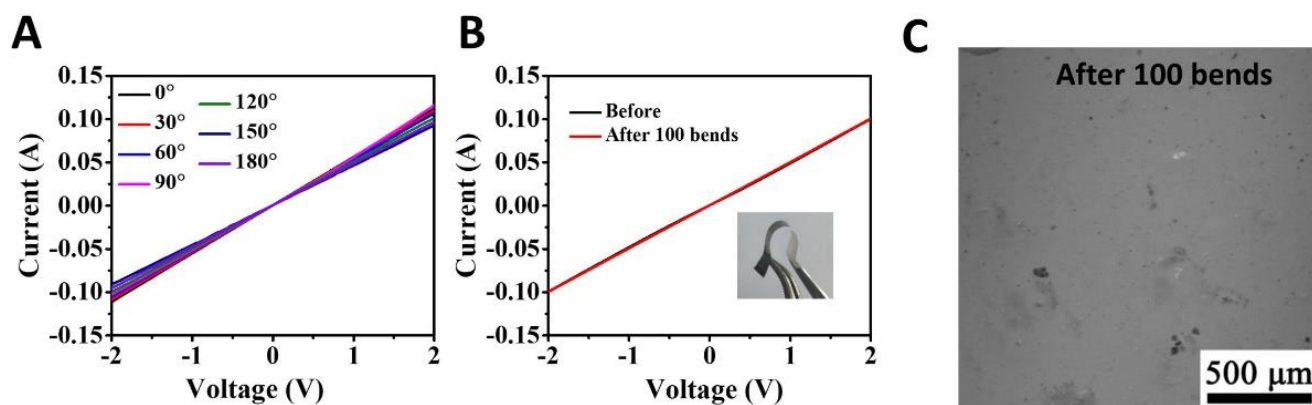


Figure S16. (A) Current-voltage (I-V) behaviours of mesoporous Au foam measured under different bending angles. CV curve(B) and surface SEM image(C) of mesoporous Au foam after 100 times bends.

References

- S1. Herrmann, A. K.; Formanek, P.; Borchardt, L.; Klose, M.; Giebeler, L.; Eckert, J.; Kaskel, S.; Gaponik, N.; Eychmüller, A. Multimetallic Aerogels by Template-Free Self-Assembly of Au, Ag, Pt, and Pd Nanoparticles. *Chem. Mater.* **2013**, 26, 1074-1083.