Supporting Information

Green Synthesis of Noble Metal Nanoparticles Using Cysteine-modified Silk Fibroin: Catalysis and Antibacterial Activity

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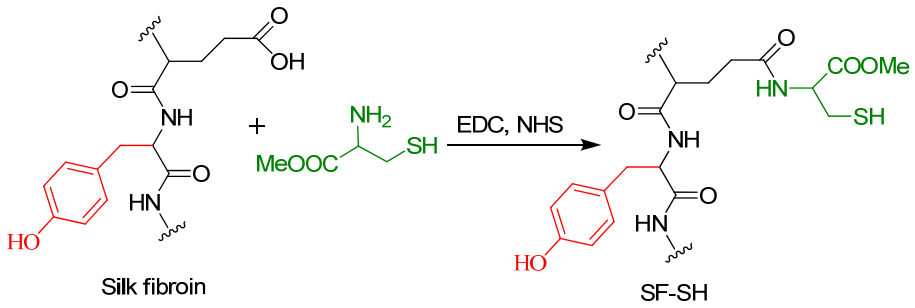
Synthesis of cysteine modified silk fibroin (SF-SH)

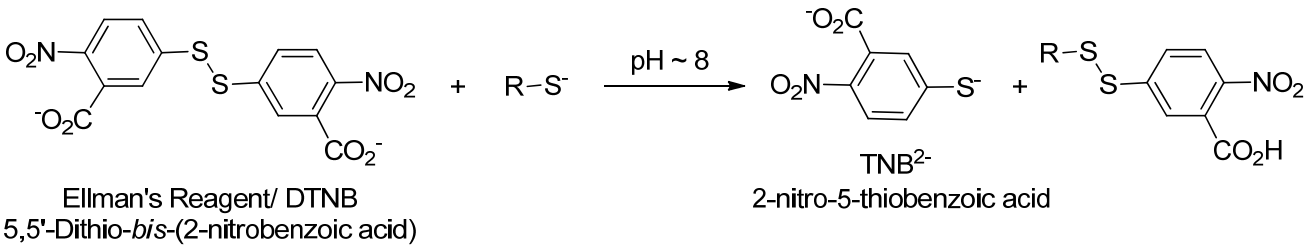
Cysteine was incorporated into SF by using EDC-NHS coupling with the aspartic and glutamic acid residue of SF. At first, the regenerated SF solution was dialyzed against PBS buffer (pH 6.5) for one day with one time change in buffer. EDC-Cl (50 equivalent) and NHS (50 equivalent) were added to that SF solution (2 wt%) in PBS buffer and the reaction mixture was stirred for five minutes at room temperature. Then Cysteine methyl ester (50 equivalents) was added into that and the reaction was allowed to proceed for two hours. After the reaction was complete, the resulting SF-SH was purified by sephadex size exclusion columns (NAP-25, GE Healthcare) pre-equilibrated with distilled water. This SF-SH was immediately used for nanoparticle synthesis; otherwise, it would have transformed into a gel after six to eight hours in air.



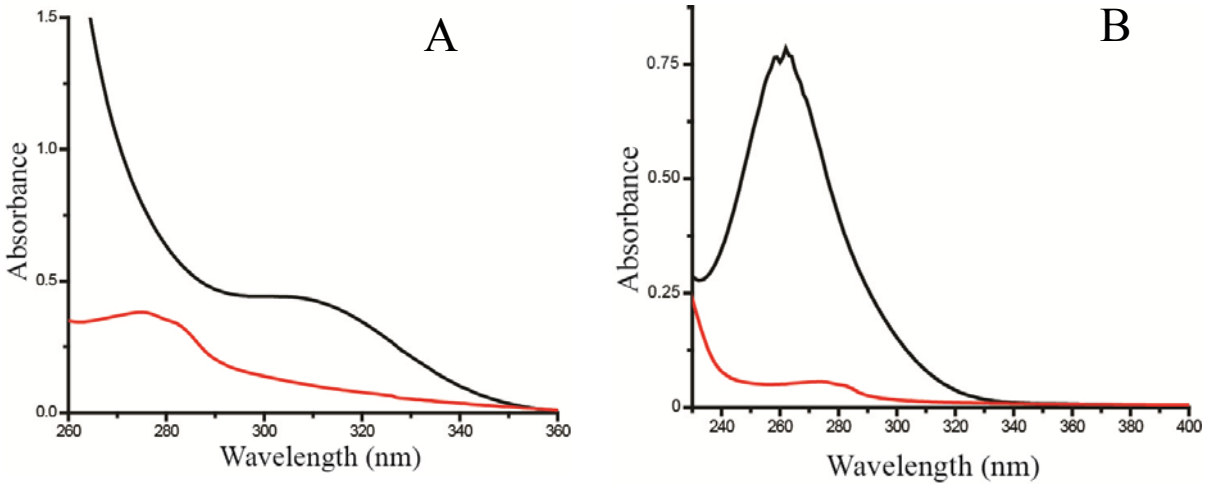
ESI Fig. 1. Synthesis of cysteine-modified silk fibroin.

Estimation of the amount of sulfhydryl group present in SF-SH

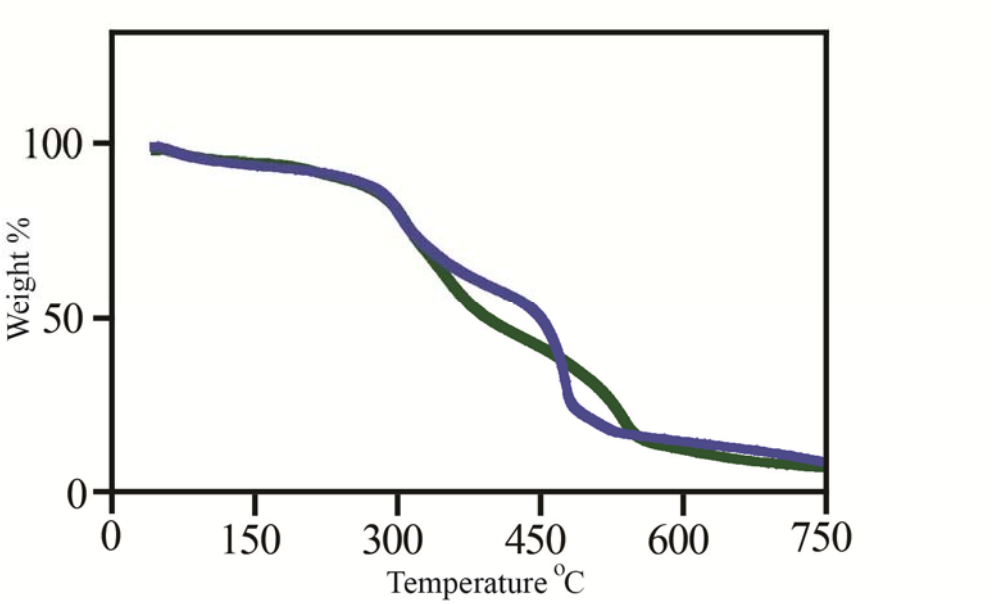
Quantitative estimation of -SH group was done spectrophotometrically using Ellman's reagent (DTNB, 5, 5'-Dithio-*bis*-(2-nitro benzoic acid)). [1] DTNB reacts with free thiol moiety (-SH) to yield 2-nitro-5-thiobenzoic acid (TNB) which shows strong absorbance at 412 nm (Ɛ = 14,150 $M^{-1}cm^{-1}$ at pH ~8. Reaction buffer of pH 8.0 was prepared using 0.1 M sodium phosphate, containing 1 mM EDTA. For optical measurement experiment, a 250 µL of SF-SH (2wt%) was mixed with 700 µL of reaction buffer and 50 µL of Ellman's reagent solution (4 mg in 1 mL of reaction buffer) and absorbance was measured. Results show more than six equivalents free-SH moiety present in SF-SH compared to normal SF.



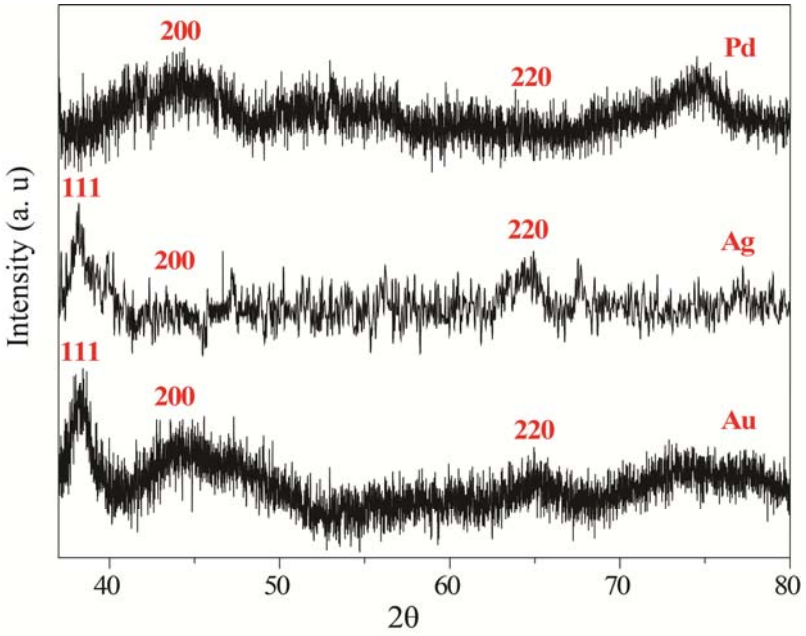
ESI Fig. 2. Detection of thiol (-SH) by using Ellman's reagent



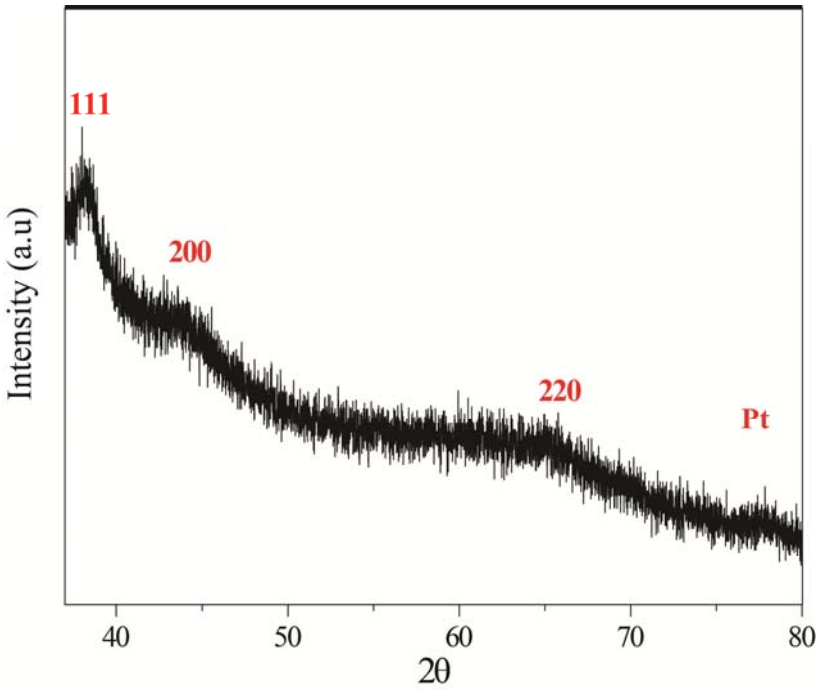
ESI Fig. 3. UV-Vis spectra of Pd (A) and Pt (B) NP synthesized by SF-SH**.** Black line indicating only metal salts in water and red line indicating after reduction by SF-SH.



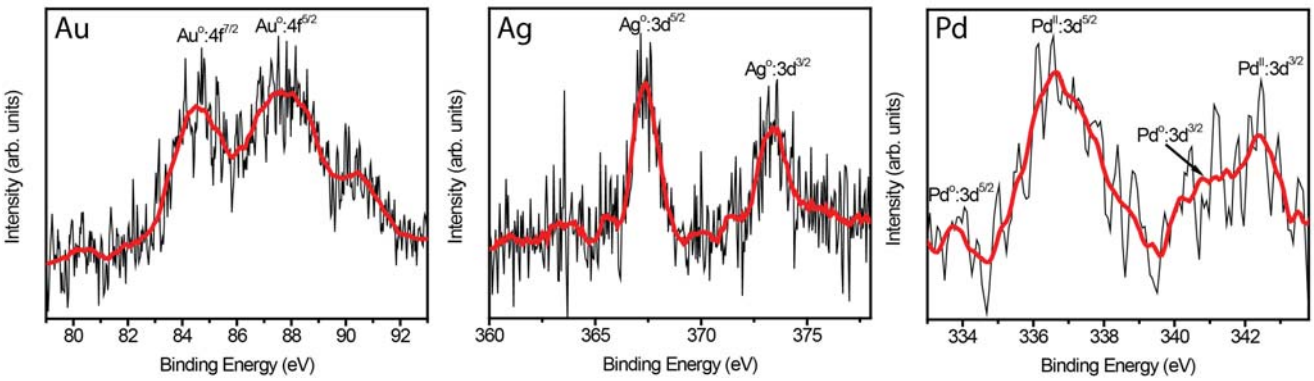
ESI Fig. 4. Thermogravimetric analysis of Ag-SF-SH (blue) and Pd-SF-SH (green).



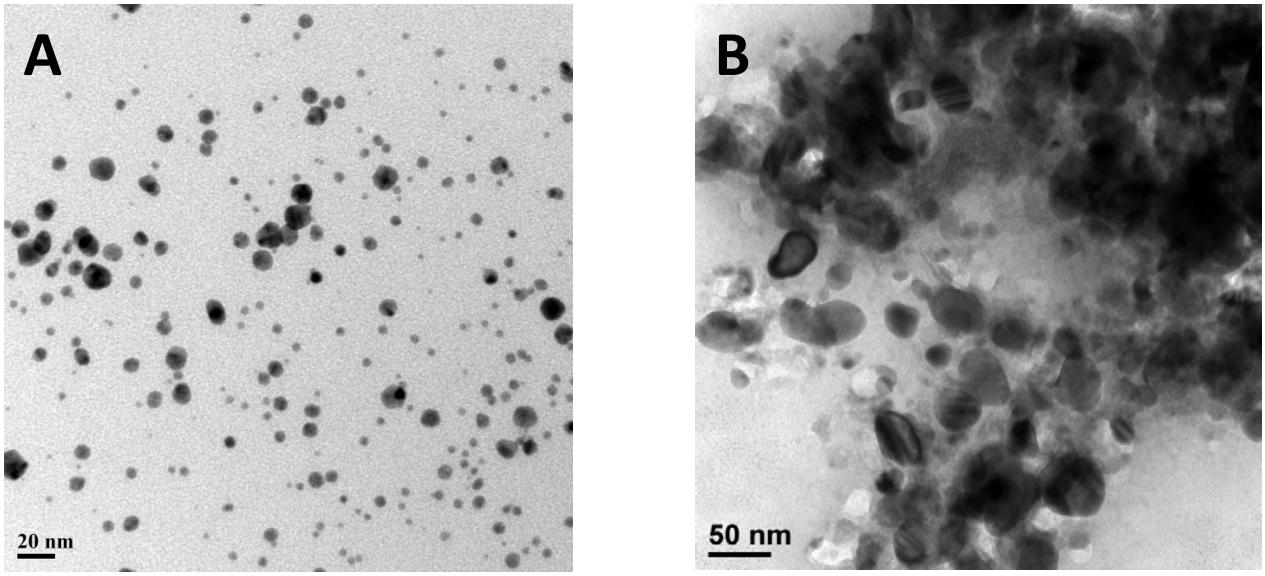
ESI Fig. 5. XRD pattern of Au, Ag and Pd NP's synthesized by SF-SH**.**



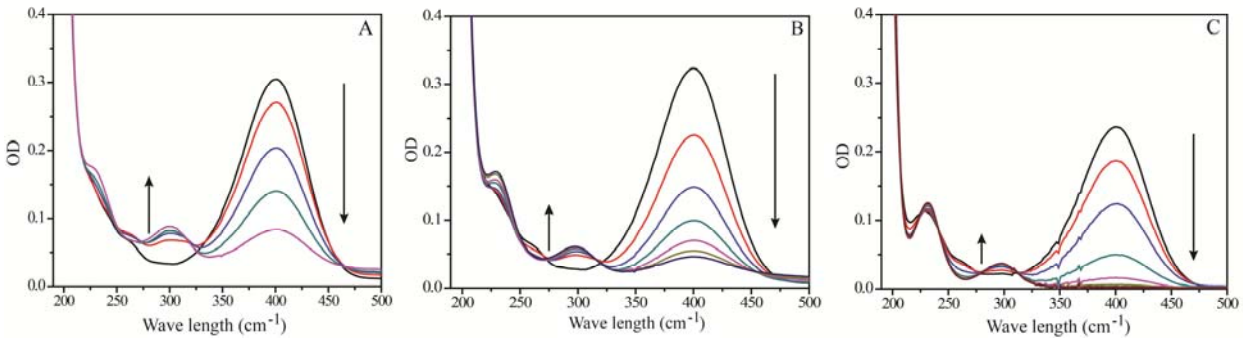
ESI Fig. 6. XRD pattern of Pt NP's synthesized by SF-SH**.**



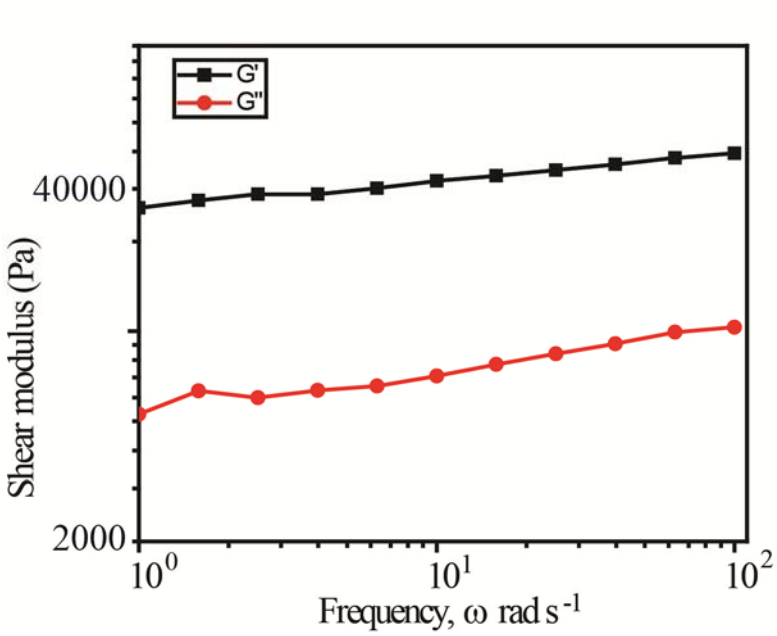
ESI Fig. 7. XPS spectra of NP-SF conjugates**.**



ESI Fig. 8. TEM micrograph of Au NPs (A) and Ag NPs (B) synthesized by normal SF.



ESI Fig. 9. Spectral kinetics scans for reduction of 4-nitrophenol by $NaBH_4$ in presence of Au (A), Ag (B), Pd (C) and NPs.



ESI Fig. 10. Rheology study was done using Au-SF-SH scaffold in water, frequency sweep of scaffold @ 0.25% strain.

ESI Fig. 11. Only SF-SH film shows no anti-bacterial activity.

Reference:

G. L. Elman *Archives of Biochemistry and Biophysics*, 1958, **74**, 443-450.