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Electronic Supplementary Information

The Fabrication of Plasmonic Nanoparticle-Containing Multilayer Films via a Bio-inspired Polydopamine Coating

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Experimental Procedure

Fabrication of (PDOP/NP) multilayer films

Prior to multilayer film deposition, glass slides or silicon wafers were cleaned by sonicating in ethanol and acetone for 10 min, respectively. Afterwards, the surfaces were then transferred into a mixture of H_2SO_4 and H_2O_2 having a volume ratio of 3:1 for 60 min, and washed with water, and kept in ethanol until the next step. Before the film deposition the surfaces were dried with N_2 gas flow.

For the deposition of PDOP layer, firstly, the slides were immersed into a dopamine solution (**dopamine hydrochloride (Sigma H8502),** 2 mg mL^{-1} in 10 mM Tris buffer, pH 8.5) at room temperature for 3 h. Then, the slides were rinsed with water and dried with N_2 gas. Finally, PDOP coated slides were treated with chloroauric acid solution (0.1 mg mL^{-1}) for 12 h to grow NPs along the surface. Additional PDOP and gold nanoparticle layers were produced by simply repeating the same cycle. To obtain general terminology for this study, n (ranging from 1 to 3) corresponded to the number of (PDOP/AuNP) layers (shown as $(PDOP/AuNP)_n$). For the comparison, PDOP coated slides were also immersed into citrate-stabilized AuNPs (cit-AuNPs) with ~20 nm diameter for 12 h. The synthesis of AuNPs was given elsewhere.[1] The same procedure was applied to create cit-AuNPs incorporated multilayer films (shown as $(PDOP/cit\text{-}AuNP)_n$)

Characterization

The UV-Vis absorption spectra of PDOP/NP multilayer films were obtained by using a Shimadzu 2600 UV–Vis–near-IR recording spectrophotometer. Scanning electron microscopy (SEM) images were recorded with a QUANTA 400F Field Emission SEM instrument. The X-Ray photoelectron spectroscopy (XPS) of the PDOP/NP

multilayer films on a silicon wafer was also performed using an SPECS EA 300 equipped with a monochromatic Al-Kα X-ray source. The size distributions, densities and surface coverage of nanoparticles were calculated via freeware IMAGEJ software.

SERS measurements

For all SERS measurements, a Delta Nu Examiner Raman Microscopy instrument equipped with a 785 nm laser source, a motorized microscope stage sample holder, and a cooled charge-coupled device (CCD) detector was employed in the range of 200–2000 cm^{-1}. The Raman instrument operating parameters were as follows: 20X objective, 3 μm spot size, 30 s acquisition time, and 150 mW laser power. Baseline correction was applied to all SERS measurements. Methylene blue (MB) was selected as the Raman reporter molecule to evaluate SERS performances of different substrates. For this, 3 μL of 1 mM aqueous solution of MB was dropped onto the PDOP/AuNP multilayer films and kept in a hood until dry. The drying procedure created coin shaped Raman sample sizes of 4±1 mm onto the multilayer films. To evaluate the reproducibility and homogeneity of SERS substrates, at least ten Raman spectra were collected from the different spots of the substrate for each sample.

Catalytic Activity Tests

The catalytic activity of the $(PDOP/AuNP)_n$ LbL multilayer films was tested for the conversion of 4-nitrophenol (4-NP) into 4-aminophenol (4-AP). For this, LbL films having almost the same size (1 x 1 cm) was immersed into 9 mL of solution containing 1 x 10^{-4} M of 4-NP and 0.033 M of $NaBH_4$. The catalytic conversion was monitored by UV-visible spectroscopy through decrease in absorption band of p-NA centered at 381 nm and increase in absorption band of 4-AP centered at 304 nm.

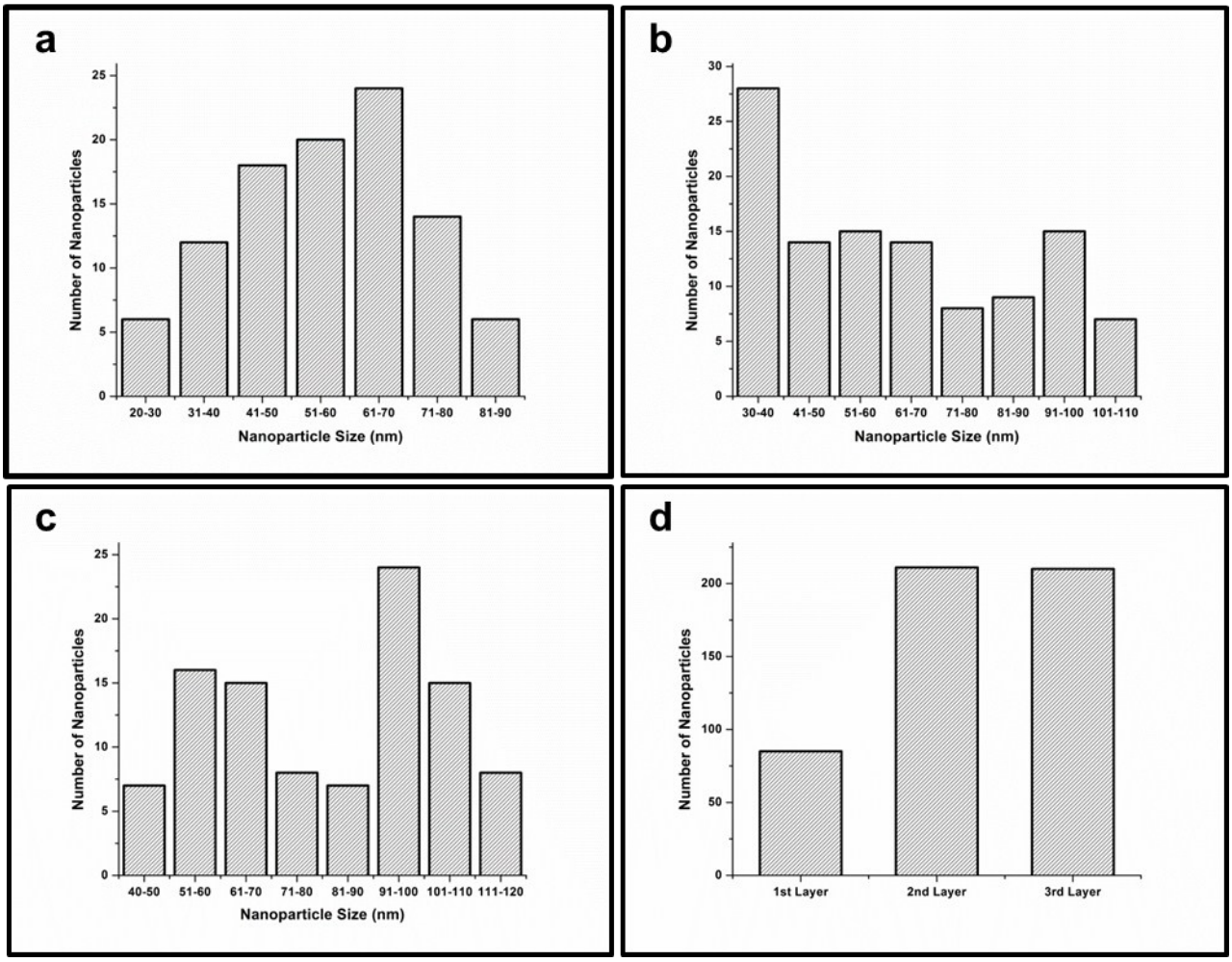

Figure S1. Height histogram of gold nanoparticles for the different layer (n) numbers of $(PDOP/AuNP)_n$ LbL films: n = 1 (a), n = 2 (b) n = 3 (c), and their nanoparticle density for the same surface area (d).

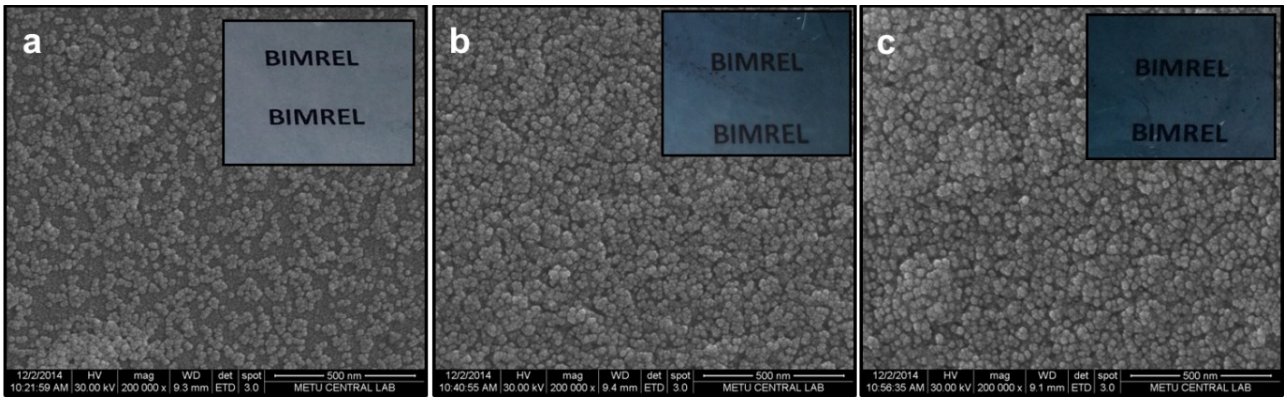

Figure S2. SEM images of citrate-stabilized gold nanoparticles and PDOP $(PDOP/cit\text{-}AuNP)_n$ LbL films for different layer (n) numbers: n = 1 (a), n = 2 (b), and n = 3 (c). The inset shows optic images of corresponding LbL films.

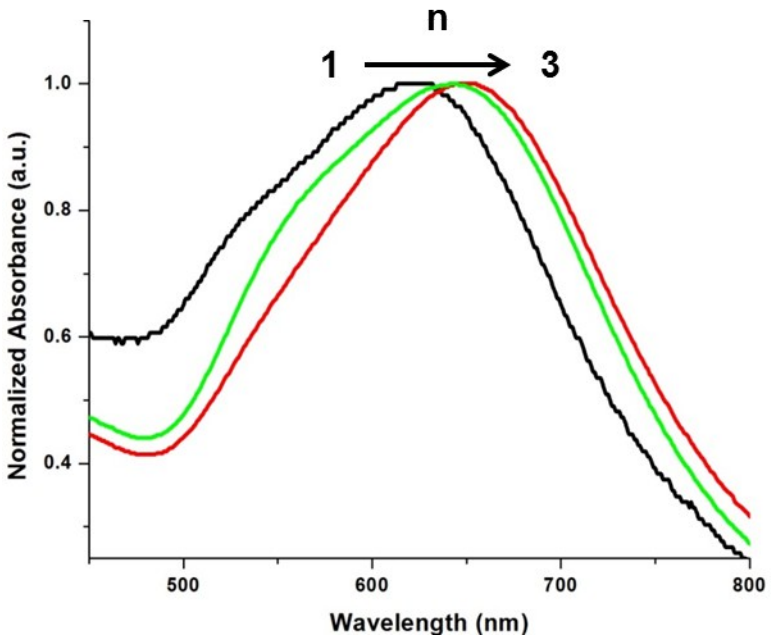

Figure S3. UV-vis spectra of $(PDOP/cit\text{-}AuNP)_n$ LbL films with n of 1, 2, and 3, respectively.

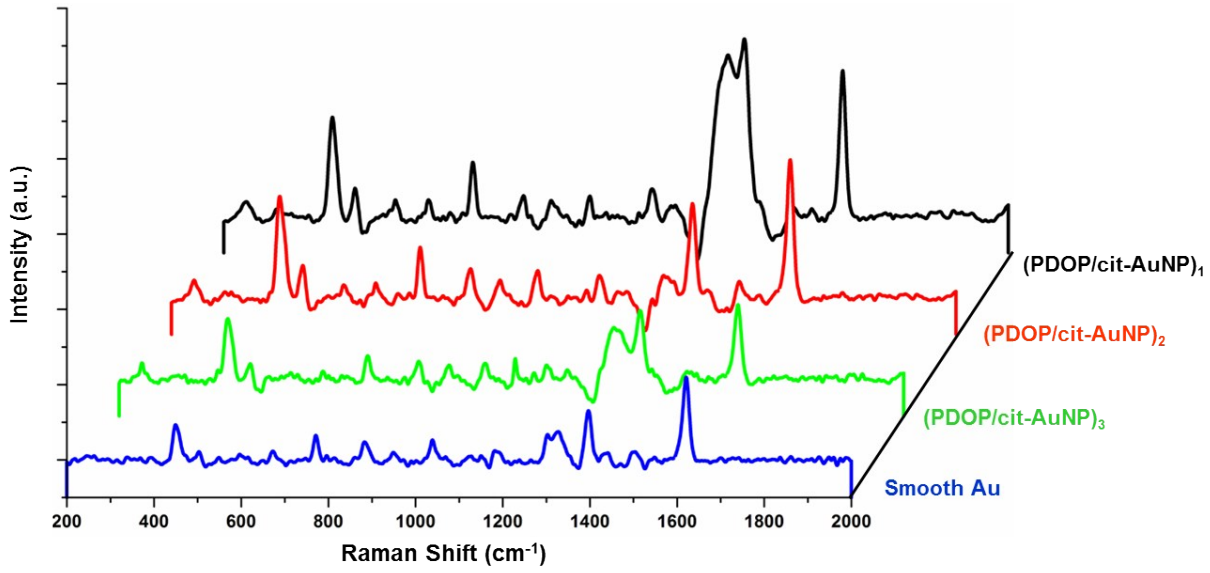

Figure S4. Representative SERS spectra of MB on the $(PDOP/cit\text{-}AuNP)_n$ LbL thin films with different layer (n) numbers.

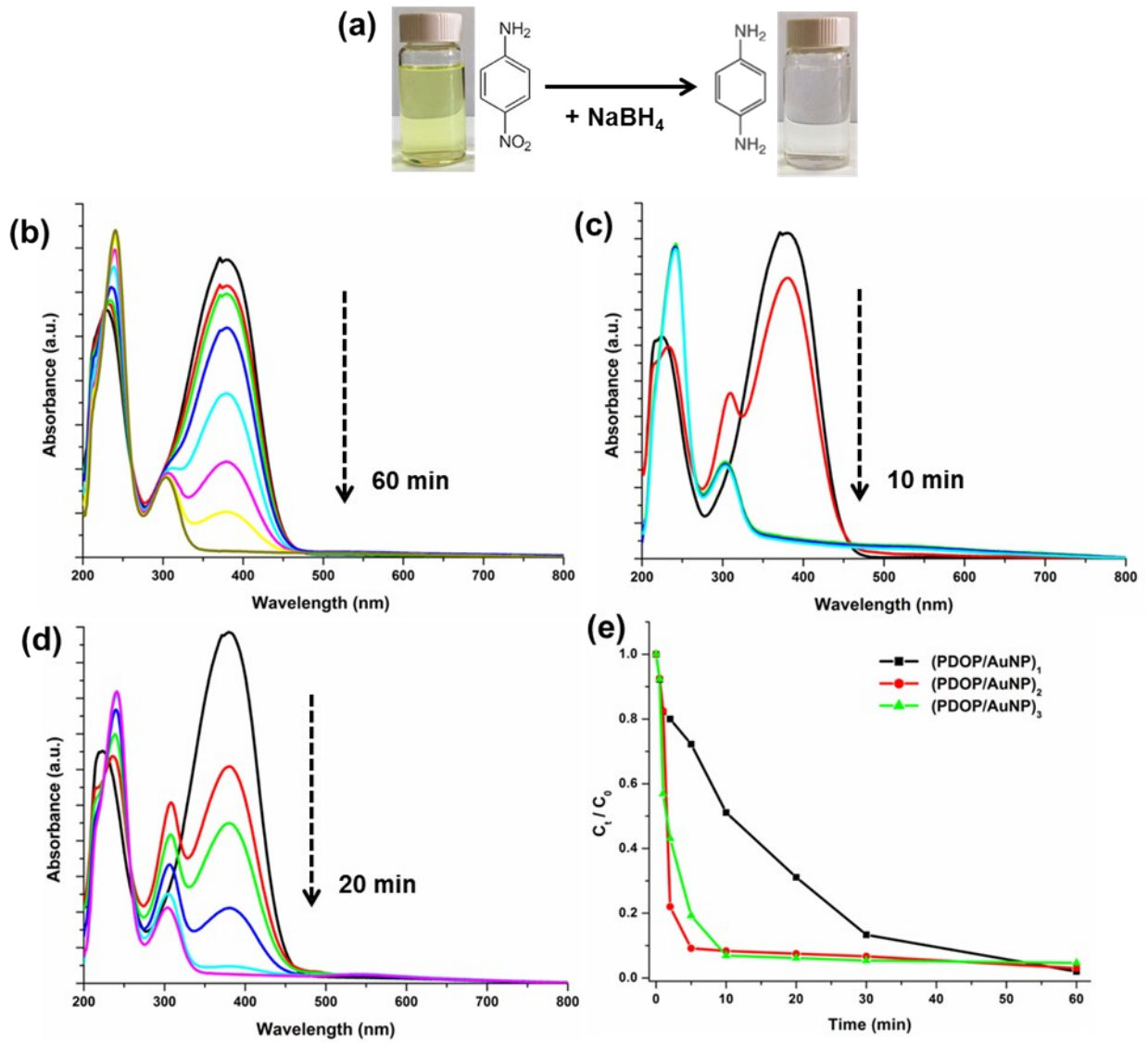

Figure S5. Schematic representation of the catalytic conversion process using AuNP incorporated multilayer films (a) and time evolution of the UV-vis spectra, showing the conversion of 4-NP to 4-AP for $(PDOP/NP)_n$ LbL thin films with different layer (n) numbers: n = 1 (b), n = 2 (c), and n = 3 (e) and kinetic trace of concentration for the same LbL films for the comparison (e).

REFERENCES

1- Jana, N. R.; Gearheart, L.; Murphy, C. J. Seeding Growth for Size Control of 5−40 nm Diameter Gold Nanoparticles. Langmuir 2001, 17, 6782−6786.