Electronic Supplementary Material (ESI) for Analytical Methods.

Surface enhanced Raman scattering active worm-like Ag clusters for sensitive and selective detection of dopamine

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1) SEM images for Ag films prepared under different sputtering time.

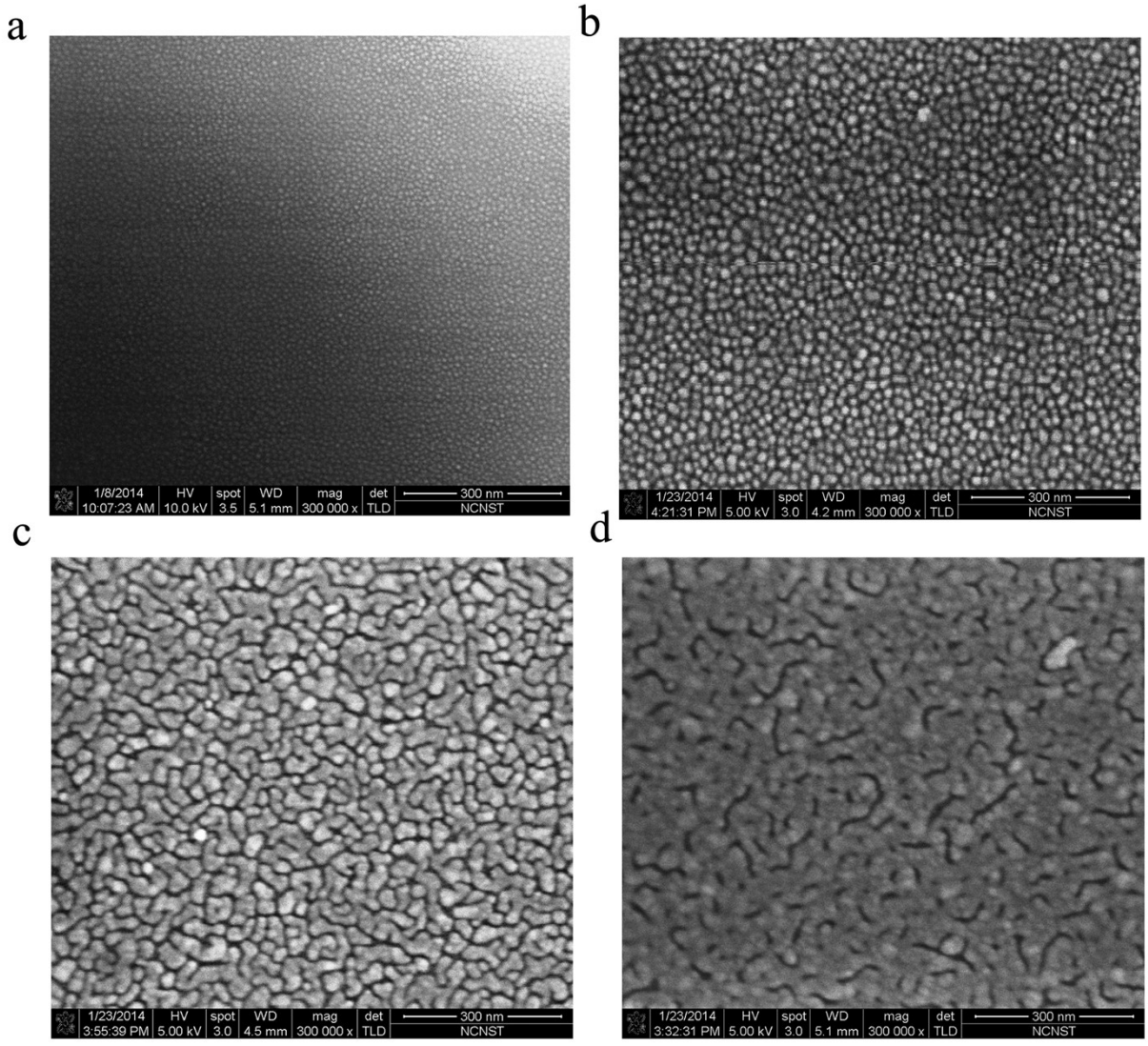

Fig. S1 SEM images for Ag films prepared under (a) 5, (b) 40, (c) 80 and (d) 120 s sputtering time

2) Ellipsometric delta and psi fitting for Ag films prepared under different sputtering time

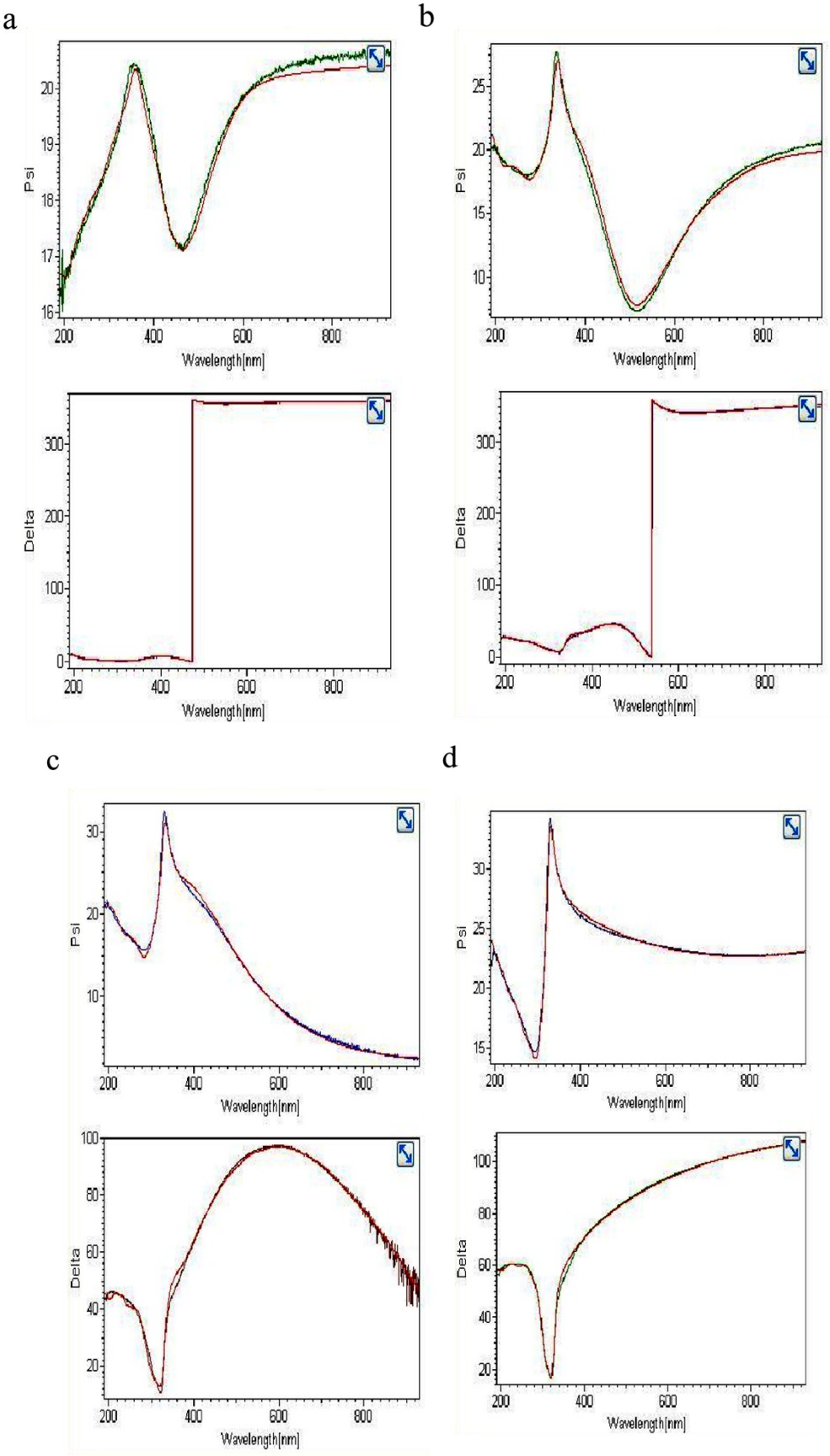

Fig. S2 Ellipsometric fitting of delta and psi for Ag films prepared under (a) 5, (b) 40, (c) 80 and (d) 120 s sputtering time

3) SERS spectra for Ag film prepared under different sputtering time in the presence of 10.0 μM DA

Table S1 SERS characteristic peaks for DA adsorbed Ag film

Raman band (cm^{-1})	Functional groups
148, 239	*V*(Ag-O)
480	*V*(Ag-O-Ag)
614, 692	*V*(C-C)
822, 1054	*V*(C-O-C)
880	*V*(O-O)
1318, 1523	*V*(C_6H_6)

Abbreviations; *V*(Ag-O): Ag-O vibration, *V*(Ag-O-Ag): Ag-O-Ag vibration, *V*(C-C): aliphatic carbon chain vibration, *V*(C-O-C): C-O-C vibration, *V*(O-O): O-O vibration and *V*(C_6H_6): benzene ring vibration.

4) SEM images for Ag films prepared under different pressure.

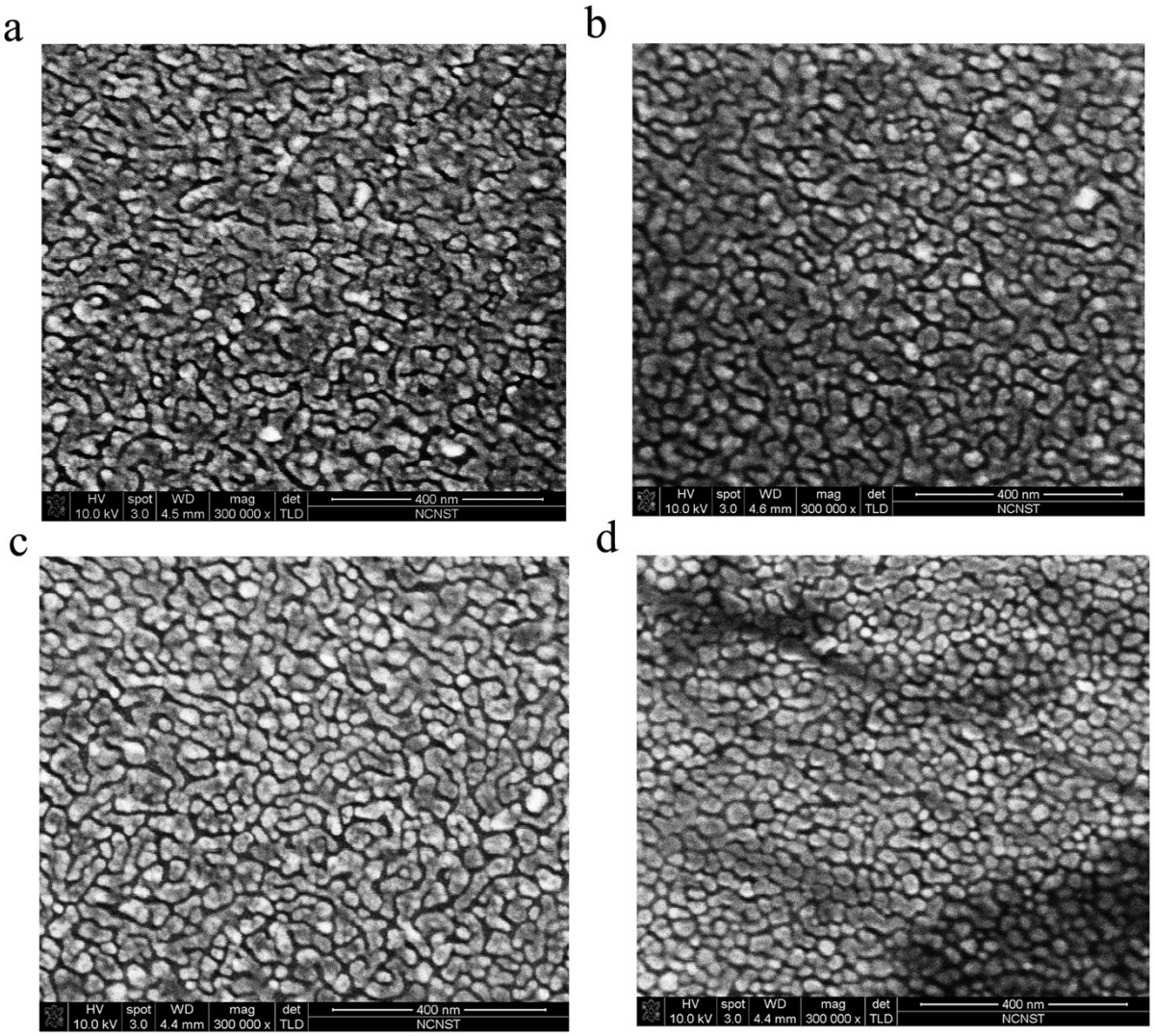

Fig. S3 SEM images for Ag films prepared under (a) 4, (b) 6, (c) 8 and (d) 12 mTorr pressure.

5) Ellipsometric delta and psi fitting for Ag films prepared under different pressure

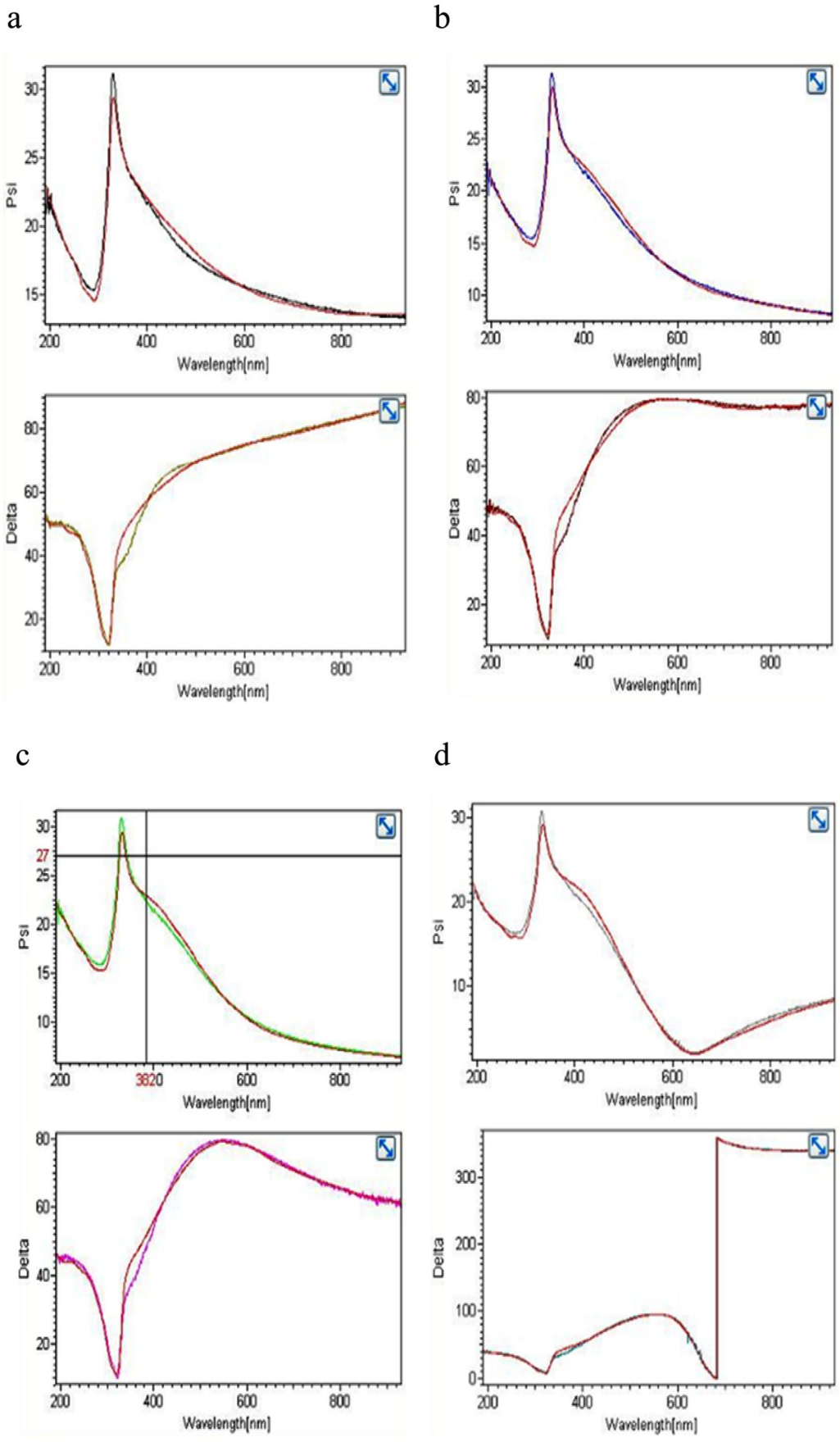

Fig. S4 Ellipsometric fitting of delta and psi for Ag films prepared under (a) 4, (b) 6, (c) 8 and ((d) 12 mTorr pressure

6) SEM images for Ag films prepared under different RF power

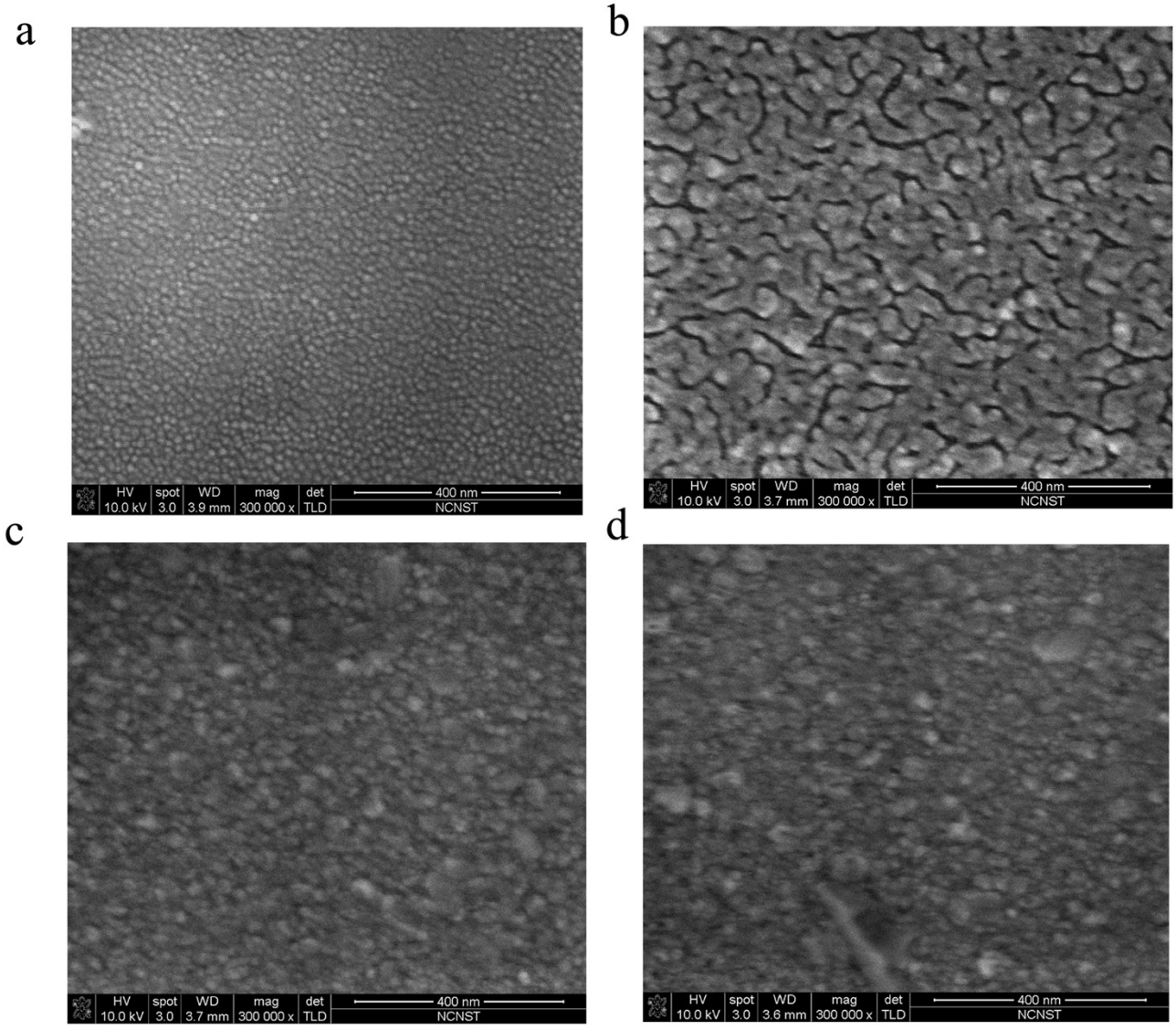

Fig. S5 SEM images for Ag films prepared under (a) 25, (b) 75, (c) 100 and (d) 125 W RF power.

7) Ellipsometric delta and psi fitting for Ag films prepared under different RF power

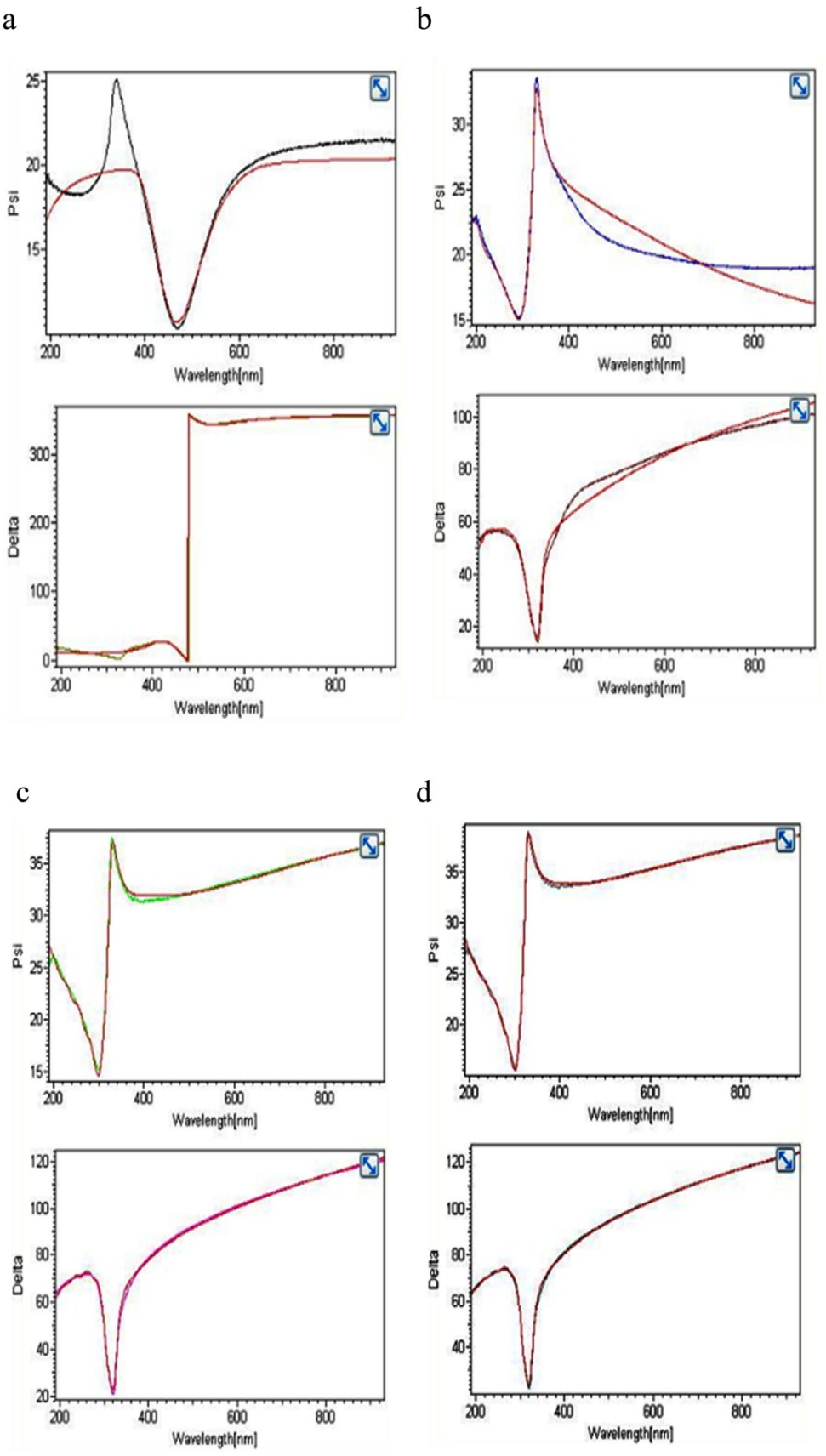

Fig. S6 Ellipsometric fitting of delta and psi for Ag films prepared under (a) 25, (b) 75, (c) 100 and (d) 125 W RF power.

8) Calculation of the enhancement factor

The enhancement factor of the SERS substrate can be calculated through the following equation [18].

$EF = (I_{SERS} \times N_{RS}) / (I_{RS} \times N_{SERS})$

Where,

EF – Enhancement factor of the SERS substrate

I_{SERS} – Intensity of the strongest peak in the SERS spectra

I_{RS} – Intensity of the same peak (as observed in the SERS spectra) for the normal Raman spectra

N_{SERS} – Number of molecules adsorbed on the scattering volume for the SERS spectra

N_{RS} – Number of molecules in the scattering volume for the normal Raman spectra (not necessary to be adsorbed)

Enhancement factor of worm-like Ag clusters modified substrate

Here, we employed the strongest peak at 1523 cm^{-1} to estimate the EF of worm-like Ag clusters modified substrate.

Observed peak intensity at 1523 cm^{-1} for the SERS spectra (I_{SERS}) = 29403

Observed peak intensity at 1523 cm^{-1} for the normal Raman spectra (I_{RS}) = 14111

Observed number of molecules adsorbed on the scattering volume for SERS spectra (N_{SERS}) = $C_{SERS} \times V_{SERS}$

Where,

C_{SERS} – the concentration of molecules used for the SERS spectra (10×10^{-6} M)

V_{SERS} – Scattering volume which contributed in the SERS spectra of molecule. This is equal to the number of worm-like Ag clusters deposited on the glass substrate. Here, it is assumed that the worm-like Ag clusters were deposited on the glass substrate as a monolayer.

That means the total scattering volume (V_{SERS}) = surface area of the substrate × size of worm-like Ag cluster

$= 0.5\ cm^2 \times 38\ nm = 0.5 \times 10^{-4} \times 38 \times 10^{-9} = 1.9 \times 10^{-12}\ m$

Therefore, $N_{SERS} = 10 \times 10^{-6} \times 1.9 \times 10^{-12} = 1.9 \times 10^{-17}$

Observed number of molecules adsorbed on the scattering volume for the normal Raman spectra (N_{RS}) = $C_{RS} \times V_{RS}$

Where,

C_{RS} – the concentration of molecules used for the normal Raman spectra (10×10^{-6} M)

V_{RS} – Scattering volume which contributed in the normal Raman spectra of molecule. This is equal to the surface area of the substrate that we have used for the Raman measurement (0.5×10^{-4} m).

Therefore, $N_{RS} = 10 \times 10^{-6} \times 0.5 \times 10^{-4} = 5 \times 10^{-10}$

Now, the EF of worm-like Ag clusters modified substrate is

$= (29403 \times 5 \times 10^{-10}) / (14111 \times 1.9 \times 10^{-17}) = \mathbf{5.4 \times 10^{7}}$

Enhancement factor for the Ag NPs@Citrate deposited on the scaffold of worm-like Ag clusters modified substrate

Observed peak intensity at 1523 cm^{-1} for the SERS spectra (I_{SERS}) = 31626

Observed peak intensity at 1523 cm^{-1} for the normal Raman spectra (I_{RS}) = 29403

Observed number of molecules adsorbed on the scattering volume for the SERS spectra (N_{SERS}) = $C_{SERS} \times V_{SERS}$

Where,

C_{SERS} – the concentration of molecules used for the SERS spectra (10×10^{-6} M)

V_{SERS} – Scattering volume which contributed in the SERS spectra of molecule. This is equal to the number of Ag NPs@Citrate deposited on the scaffold of worm-like Ag clusters modified substrate. Here, it is assumed that the Ag NPs@Citrate was deposited on the scaffold of worm-like clusters modified substrate as a monolayer.

That means the total scattering volume (V_{SERS}) = surface area of the substrate × the size of worm-like Ag cluster × the size of Ag NPs@Citrate

$= 0.5\ cm^2 \times 38\ nm \times 28\ nm = 0.5 \times 10^{-4} \times 38 \times 10^{-9} \times 28 \times 10^{-9} = 5.3 \times 10^{-20}\ m$

Therefore, $N_{SERS} = 10 \times 10^{-6} \times 5.3 \times 10^{-20} = 5.3 \times 10^{-25}$

Observed number of molecules adsorbed on the scattering volume for the normal Raman spectra (N_{RS}) = $C_{RS} \times V_{RS}$

Where,

C_{RS} – the concentration of molecules used for the normal Raman spectra (10×10^{-6} M)

V_{RS} – Scattering volume which contributed in the normal Raman spectra of molecule. This is equal to the number of worm-like Ag clusters deposited on the glass substrate.

That means the total scattering volume (V_{RS}) = surface area of the substrate × the size of Ag cluster

$= 0.5\ cm^2 \times 38\ nm = 0.5 \times 10^{-4} \times 38 \times 10^{-9} = 1.9 \times 10^{-12}\ m$

Therefore, $N_{RS} = 10 \times 10^{-6} \times 1.9 \times 10^{-12} = 1.9 \times 10^{-17}$

Now, the EF for Ag NPs@Citrate deposited on the scaffold of worm-like Ag clusters modified substrate is

$= (31626 \times 1.9 \times 10^{-17}) / (29403 \times 5.3 \times 10^{-25}) = \mathbf{3.8 \times 10^{7}}$

Enhancement factor for the Ag NPs@Citrate-BDT deposited on the scaffold of worm-like Ag clusters modified substrate

Observed peak intensity at 1523 cm^{-1} for the SERS spectra (I_{SERS}) = 69719

Observed peak intensity at 1523 cm^{-1} for the normal Raman spectra (I_{RS}) = 29403

Observed number of molecules adsorbed on the scattering volume for the SERS spectra (N_{SERS}) = $C_{SERS} \times V_{SERS}$

Where,

C_{SERS} – the concentration of molecules used for the SERS spectra (10×10^{-6} M)

V_{SERS} – Scattering volume which contributed in the SERS spectra of molecule. This is equal to the number of Ag NPs@Citrate-BDT deposited on the scaffold of worm-like Ag clusters modified substrate. Here, it is assumed that the Ag NPs@Citrate-BDT was deposited on the scaffold of worm-like Ag clusters modified substrate as a monolayer.

That means the total scattering volume (V_{SERS}) = surface area of the substrate × the size of Ag cluster × the size of Ag NPs@Citrate-BDT

$$= 0.5 \text{ cm}^2 \times 38 \text{ nm} \times 35 \text{ nm} = 0.5 \times 10^{-4} \times 38 \times 10^{-9} \times 35 \times 10^{-9} = 6.6 \times 10^{-20} \text{ m}$$

Therefore, $N_{SERS} = 10 \times 10^{-6} \times 6.6 \times 10^{-20} = 6.6 \times 10^{-25}$

Observed number of molecules adsorbed on the scattering volume for the normal Raman spectra (N_{RS}) = $C_{RS} \times V_{RS}$

Where,

C_{RS} – the concentration of molecules used for the normal Raman spectra (10×10^{-6} M)

V_{RS} – Scattering volume which contributed in the normal Raman spectra of molecule. This is equal to the number of worm-like Ag clusters deposited on the glass substrate.

That means the total scattering volume (V_{RS}) = surface area of the substrate × the size of Ag cluster

$$= 0.5 \text{ cm}^2 \times 38 \text{ nm} = 0.5 \times 10^{-4} \times 38 \times 10^{-9} = 1.9 \times 10^{-12} \text{ m}$$

Therefore, $N_{RS} = 10 \times 10^{-6} \times 1.9 \times 10^{-12} = 1.9 \times 10^{-17}$

Now, the EF for the Ag NPs@Citrate-BDT deposited on the scaffold of worm-like Ag clusters modified substrate is

$$= (69719 \times 1.9 \times 10^{-17}) / (29403 \times 6.6 \times 10^{-25}) = \mathbf{6.8 \times 10^{7}}$$