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Biomimetic Synthesis of Hierarchical 3D Ag Butterfly Wing Scales Arrays/graphene Composites as Ultrasensitive SERS Substrates for Efficient Trace Chemical Detection

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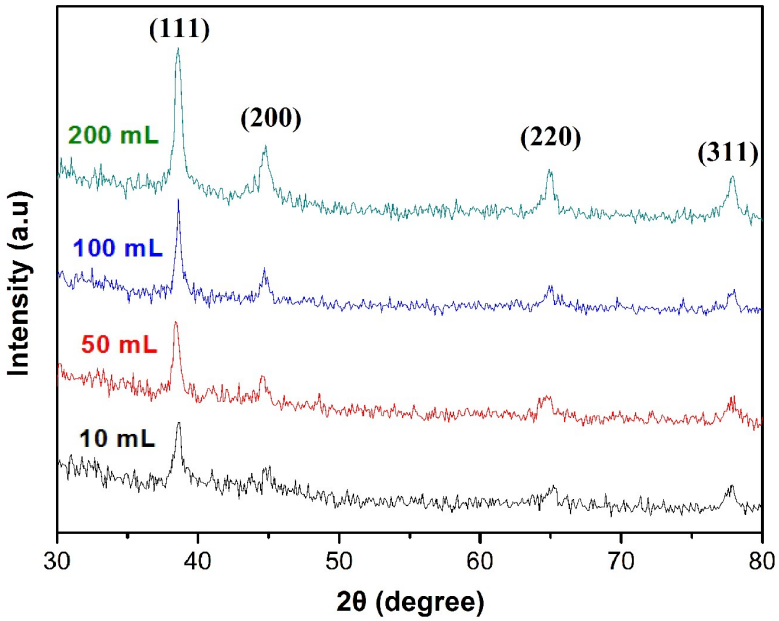

Figure S1. XRD patterns of the 3D Ag butterfly wing scales synthesized at different concentration of $AgNO_3$.

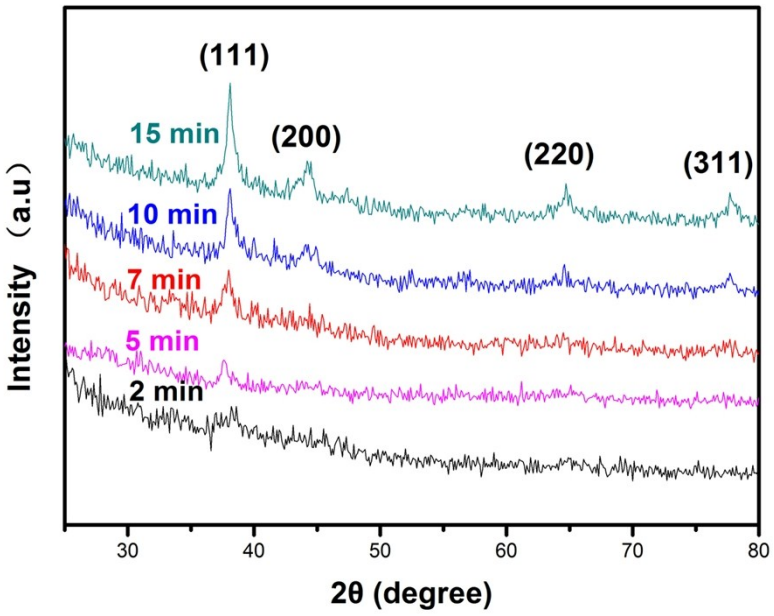

Figure S2. XRD patterns of Ag butterfly wing scale arrays prepared under different Ag coating time. The XRD pattern of the product prepared for 25 min is not shown.

Calculation of SERS enhancement factor (EF)

To quantify the enhancement contribution from graphene, we calculated the enhancement factor (EF) based on the following formula:

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

where I_{SERS} and I_{BULK} represent the intensities of SERS and normal Raman scattering, whereas N_{SERS} and N_{BULK}, respectively, denote the numbers of corresponding CV molecules effectively excited by a laser beam. According to the above formula, the EF for the Ag substrate is calculated to be 1.48×10^6. Similarly, the EF is calculated to be 4.79×10^6 for the Ag/graphene substrate. As a result, the EF for the Ag/graphene substrate shows a 3.24-fold enhancement compared to the Ag substrate. The detailed EF calculation process can be seen in the supporting information and Fig. S3.

N_{BULK} = (Laser spot area/Diffusion area) * (N_A * $Volume_{BULK}$ * $Concentration_{BULK}$)

N_{SERS} = (Laser spot area/Substrate area) * (N_A * $Volume_{SERS}$ * $Concentration_{SERS}$)

Diffusion area=$\pi(d/2)^2$=0.5027cm^2

Substrate area=0.25cm^2

$Volume_{BULK}$ =$Volume_{SERS}$

$Concentration_{BULK}$ = 10^5 * $Concentration_{SERS}$

N_{BULK} / N_{SERS}= $(0.25/0.5027) \times 10^5 = 5 \times 10^4$

I = intensity of the 1173 cm^{-1} peak

I_{BULK}=599 a.u.

$I_{SERS,Ag}$ =17823 a.u.

$I_{SERS,Ag} / I_{BULK}$=29.75

$EF = (I_{SERS} / I_{BULK}) \times (N_{BULK} / N_{SERS}) = 1.48 \times 10^6$

$I_{SERS,Ag/rGO}$ =57421 a.u.

$I_{SERS,Ag} / I_{BULK}$=95.86

$EF = (I_{SERS} / I_{BULK}) \times (N_{BULK} / N_{SERS}) = 4.79 \times 10^6$

The EF for the Ag/rGO substrate shows a 3.24-fold enhancement compared to the Ag substrate

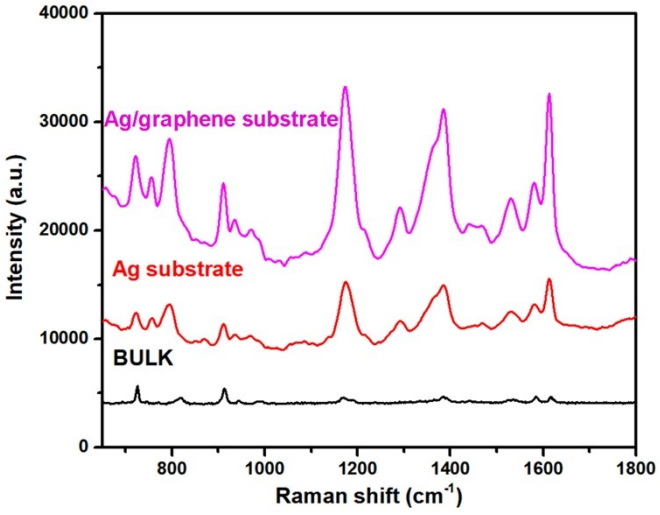

Figure S3. Raman spectrum of CV solution (10^{-1} M) and SERS spectra of CV (10^{-6} M) absorbed on Ag substrate and Ag/graphene substrate.

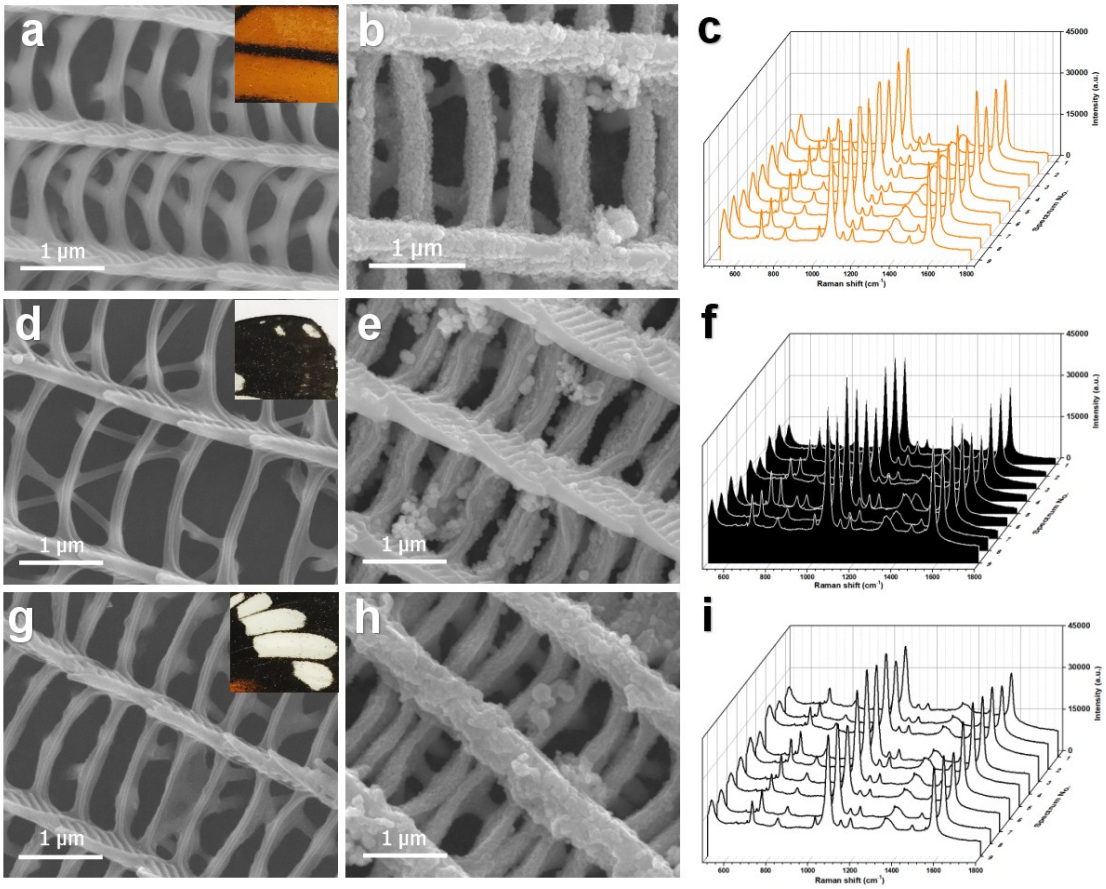

Figure S4. SEM images of (a, d, g) original wing scales in yellow, black and white respectively and (b, e, h) corresponding Ag wing scales. (c, f, i) SERS spectra of MBA (10^{-5} M) adsorbed on the substrates made from wings scales in different colors.

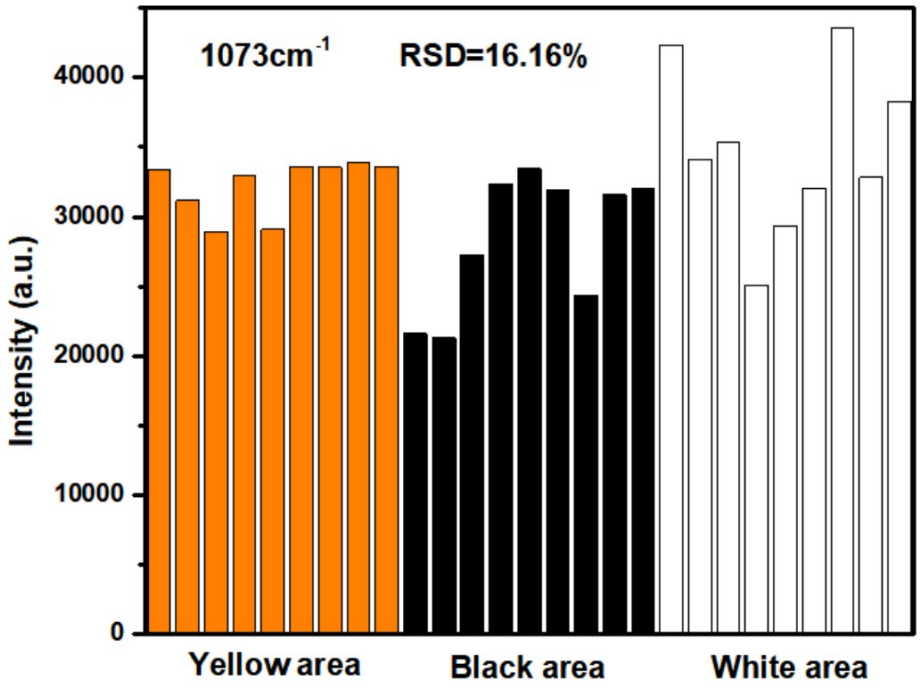

Fig. S5. Spot-to-spot intensity variations of the characteristic peak at 1073 cm^{-1} (SERS spectra of MBA molecules) for the substrates in yellow, black and white.

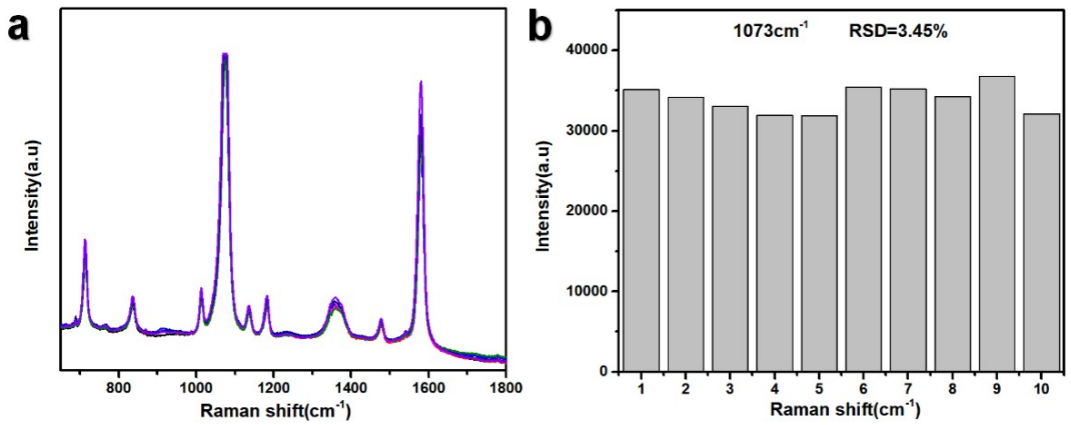

Fig. S6 (a) A series of SERS spectra of MBA molecules collected on 10 substrates fabricated from different bodies of butterflies, (b) Spot-to-spot intensity variation of the characteristic peak at 1073 cm^{-1} for the 10 substrates.