Supporting Information

Cyclic Electroplating and Stripping of Silver on Au@SiO$_2$ Core/Shell Nanoparticles for Sensitive and Recyclable Substrates of Surface-enhanced Raman Scattering

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Experimental

Synthesis of Au nanoparticles

The Au cores size of ~70 nm is synthesized by the citrate reduction of $HAuCl_4$ which is described elsewhere.[1,2] Namely, in H_2O (100 mL), 1 mL of a $HAuCl_4{\cdot}3H_2O$ solution (1% by weight) was dissolved, to which, 0.3 mL of a 1% (m/m) trisodium citrate aqueous solution was added (total volume 100 mL) with stirring. After heating at reflux for approximately 140 s, the solution turned dark red, indicating that Au nanoparticle were obtained.

Results and Discussion

SERS enhancement factor

The enhancement factor (EF) for rhodamine B (RdB) is calculated according to the following formula: [3,4]

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

where I_{SERS} and I_{bulk} are the vibration intensities in the SERS and normal Raman spectra of RdB, respectively. N_{bulk} and N_{surf} are the number of molecules under laser illumination for the bulk sample, and the number of molecules in the self-assembled monolayers (SAMs), respectively. The N_{surf} and N_{bulk} values can be calculated on the basis of the estimate of the concentration of surface species or bulk sample and the corresponding sampling areas. It is reported that the average surface density of rhodamine 6G (R6G) molecules in densely packed monolayers is approximately one R6G molecule per 4 nm^2.[5] We assumed the average surface density of RdB monolayers is 4 nm^2 since the molecular structure of RdB is similar with that of R6G. Then the surface coverage of RdB monolayer on Au@SiO$_2$@Ag nanostructures is 4.15×10^{-11} molcm^{-2} ($\Gamma=1$ / (4×10^{-14}) / (6.02×10^{23}) mol cm^{-2}=4.15×10^{-11} mol cm^{-2}). Taking the sampling area (ca. 1 μm in diameter) into account, N_{surf} has a value of 3.26×10^{-19} mol ($N_{surf}=\Gamma \times \pi \times 0.25$ μm^2=3.26×10^{-19} mol). For the solid sample, the sampling volume is the product of the area of the laser spot (ca. 1 μm diameter) and the penetration depth (~2μm) of the focused laser beam. Assuming the density of bulk RdB is 0.79 g cm^{-3}, N_{bulk} can be calculated to be 2.59×10^{-15} mol (N_{bulk}=0.79g cm^{-3} × π × 0.25 μm^2 × 2 μm / (479.01 g mol^{-1})=2.59×10^{-15} mol). For the vibrational mode at 1580 cm^{-1}, the ratio of I_{surf} to I_{bulk} 10.6, so EF was calculated to be 8.43×10^4.

The UV–Vis-NIR absorbance spectra of bare Au nanoparticles, core-shell Au@SiO_2 nanoparticles and Au@SiO_2@Ag nanostructures have been studied in Fig. S1.

Fig. S1

It is known that the Raman scattering intensity is directly proportional to the excitation power.[6] Below the threshold for sample damage, linear relationships are expected and the response of the Au@SiO_2@Ag nanostructures were examined for this behavior (as shown in Fig. S2). A linear relationship is seen in the plot of excitation power *versus* peak intensity at 1503 cm^{-1}. This data provides two important pieces of information: firstly, even at low excitation powers, the SERS signals of RdB absorbed on the Au@SiO_2@Ag nanostructures can be identified. Secondly, several fold more intense spectra can be collected by using more intense excitation sources.

Fig. S2

To further test the influence of electrodeposition time of silver on the SERS activity of Au@SiO_2@Ag nanostructures, the SERS spectra of RdB absorbed on Au@SiO_2@Ag nanostructures with different electrodeposition time of silver have been shown in Fig. S3.

Fig. S3

The possible formation mechanism for the electrodeposition of Ag on the Au@SiO_2 assembled ITO (Au@SiO_2@Ag) substrate under different electrodeposition time has been described.

Fig. S4

In order to further assess the uniformity of Au@SiO_2@Ag nanostructures, RdB as a target analyte was utilized to examine the uniformity of dried silver island substrate and Au@SiO_2@Ag nanostructures (see Fig. S5). Moreover, compare to most available SERS substrate (Au, Ag colloid, and generally oxidation-reduction-cycles (ORCs) treated Au, Ag electrode), SiO_2@Ag nanostructures, Au@Ag nanostructures, the SERS active Au@SiO_2@Ag nanostructures has a higher SERS enhancement factor in the near-infrared wavelength region as shown in Fig. S6 and Fig. S7.

Fig. S5, Fig. S6 and Fig. S7

The long-term stability and recyclability of SiO_2@Ag, Au@Ag, and the Au@SiO_2@Ag nanostructures can be evaluated by the relative SERS intensity of RdB at 1503 cm^{-1}. Based on the ITO substrate, both the SiO_2@Ag nanostructures and the Au@Ag nanostructures were prepared and served as reference for evaluating the long-term stability and recyclability of Au@SiO_2@Ag nanostructures.

Fig. S8

The reusability of the Au@SiO_2@Ag nanostructures was performed in Fig. S9. RdB, was selected to determine the surface properties of the nanostructures. The SERS intensity of RdB on the 1-nanostructures (1-nanostructures are Au@SiO_2 nanoparticles treated with 1 min of silver electrodeposition) decreased by about 10% compared to the initial amount.

Fig. S9

References

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Figure captions

Fig. S1. UV–Vis-NIR absorbance spectra of bare Au nanoparticles (a), core-shell Au@SiO_2 nanoparticles (b), and Au@SiO_2@Ag nanostructures (c).

Fig. S2. SERS spectra of RdB on Au@SiO_2@Ag nanostructures with excitation powers as labeled (a). Graph of the excitation power at the sample versus peak intensity of 1503 cm^{-1} (b). Error bar represent standard deviation of three measurements at each parameter determination. Acquisition parameters: 785-nm excitation, 10-s integrations.

Fig. S3. SERS spectra of RdB molecules on Au@SiO_2 modified ITO substrate deposited silver atom for difference times: a) 1, b)3, c) 5, d) 10, e) 30 and f) 60 min. Acquisition parameters: 150 mW of 785-nm excitation, 10-s integration.

Fig. S4. The possible formation mechanism of the electrodeposition of Ag on the Au@SiO_2 assembled (Au@SiO_2@Ag nanostructures) ITO substrate under different electrodeposition time (t).

Fig. S5. SERS spectra of RdB (1×10^{-9} M) from 6 different spots in one sample on the Au@SiO_2@Ag nanostructures (A) and a silver island film (B). The insets display SEM images of Au@SiO_2@Ag nanostructures and silver island film, respectively.

Fig. S6. SERS spectra of RdB on Ag (a) , Au (b) nanoparticles by citrate reduction, generally ORCs treated Ag (c), Au (d) electrode, and the proposed method in this paper (e).

Fig. S7. SERS spectra of RdB on Au@SiO_2 nanoparticles (a), Au nanoparticles (b), SiO_2@Ag nanostructures (c), Au@Ag nanostructures (d), and the Au@SiO_2@Ag nanostructures (e).

Fig. S8. (A) SERS spectra demonstrate the long-term stability of SiO_2@Ag, Au@Ag, and the Au@SiO_2@Ag nanostructures, respectively. (B) SERS spectra investigation of the recyclability of SiO_2@Ag, Au@Ag, and the Au@SiO_2@Ag nanostructures after 1~10 electrodeposition/stripping Ag cycles. The error bars represent typical intensity variations obtained from the same sample measured at 6 different spots.

Fig. S9. SERS spectra of RdB molecules on Au@SiO_2 modified ITO substrate deposited silver atom for 1 min (curve a) and the same substrate after 10 times renewal (curve b). The intensity ratio at 1503 cm^{-1} of curve a and b is about 1:0.87.

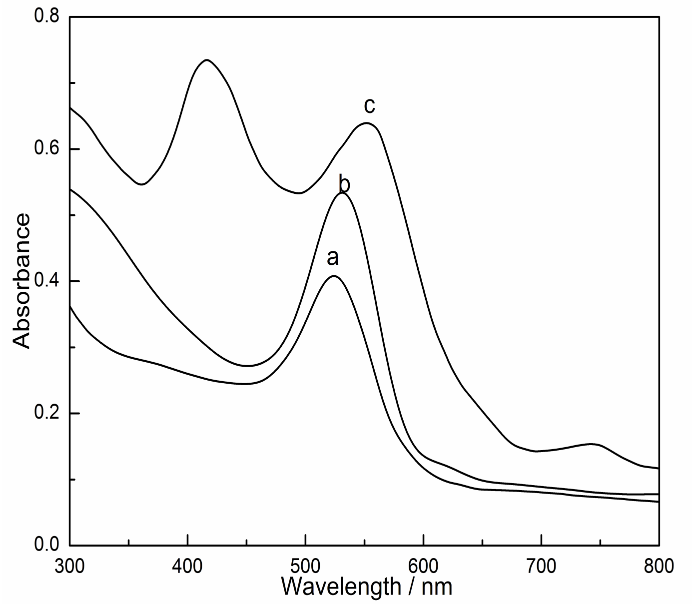

Fig. S1

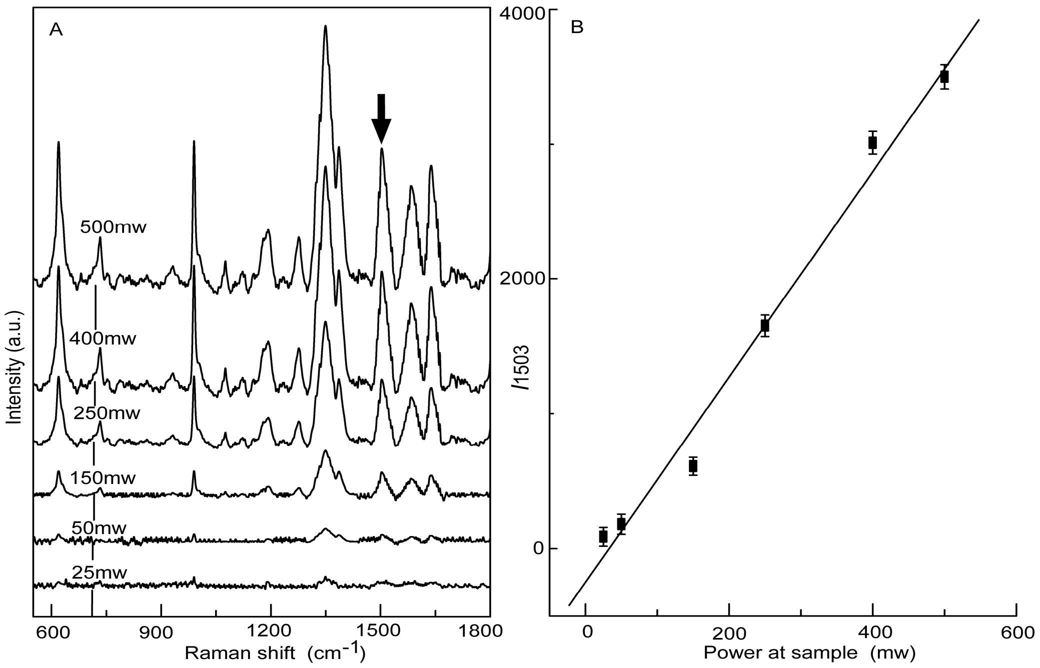
A
500mw
400mw
250mw
150mw
50mw
25mw
Intensity (a.u.)
600
900
1200
1500
1800
Raman shift (cm^{-1})
B
4000
2000
0
I_{1503}
0
200
400
600
Power at sample (mw)

Fig. S2

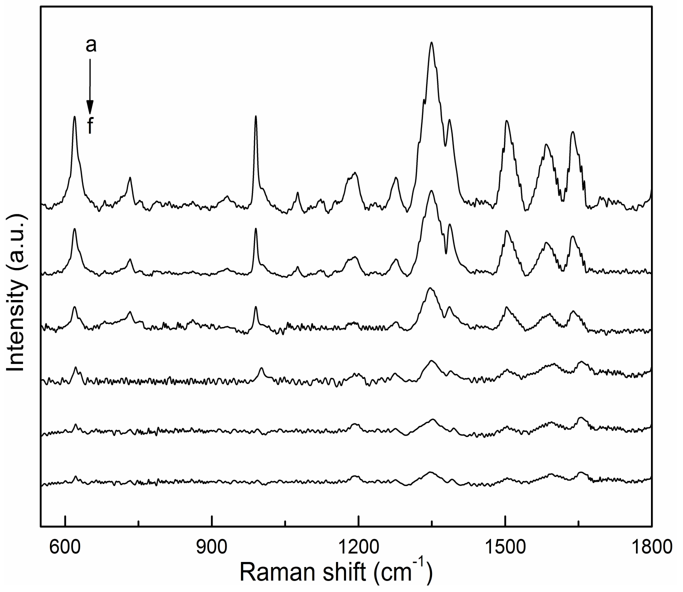
a
f
Intensity (a.u.)
600
900
1200
1500
1800
Raman shift (cm^{-1})

Fig. S3

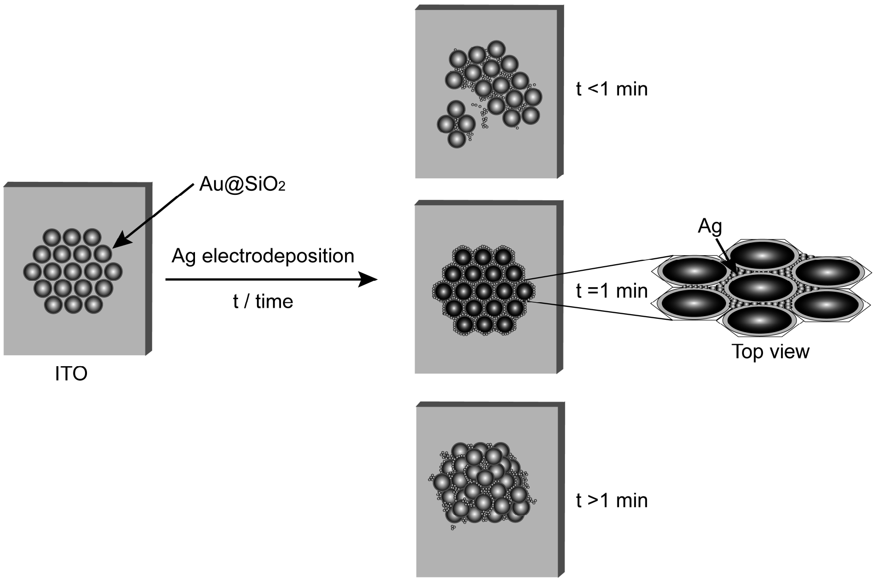
Au@SiO2
ITO
Ag electrodeposition
t / time
t <1 min
t =1 min
t >1 min
Ag
Top view

Fig. S4

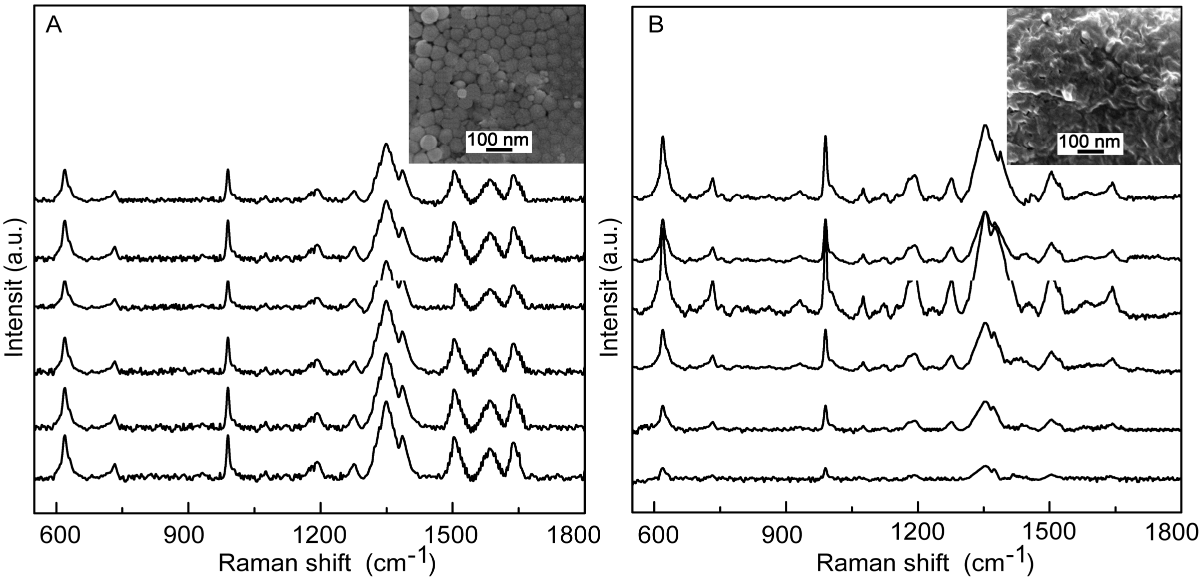
A
B
100 nm
100 nm
Intensit (a.u.)
Intensit (a.u.)
600
900
1200
1500
1800
600
900
1200
1500
1800
Raman shift (cm-1)
Raman shift (cm-1)

Fig. S5

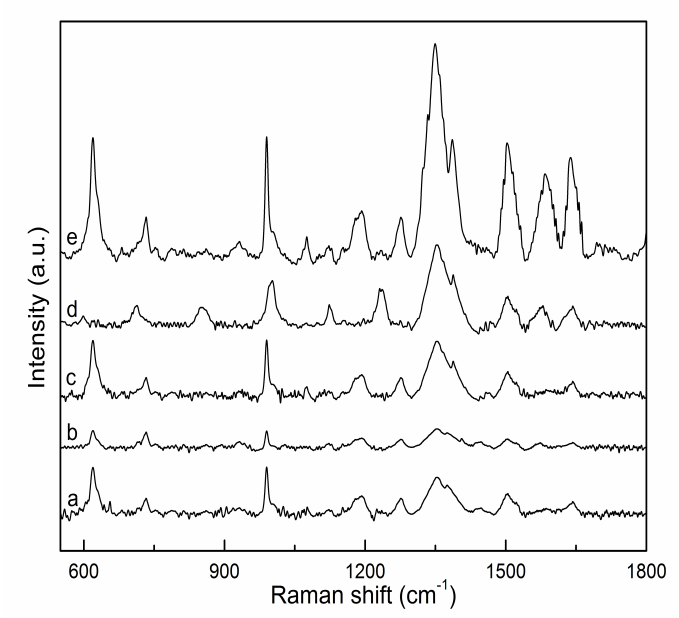
e
d
c
b
a
Intensity (a.u.)
600
900
1200
1500
1800
Raman shift (cm^{-1})

Fig. S6

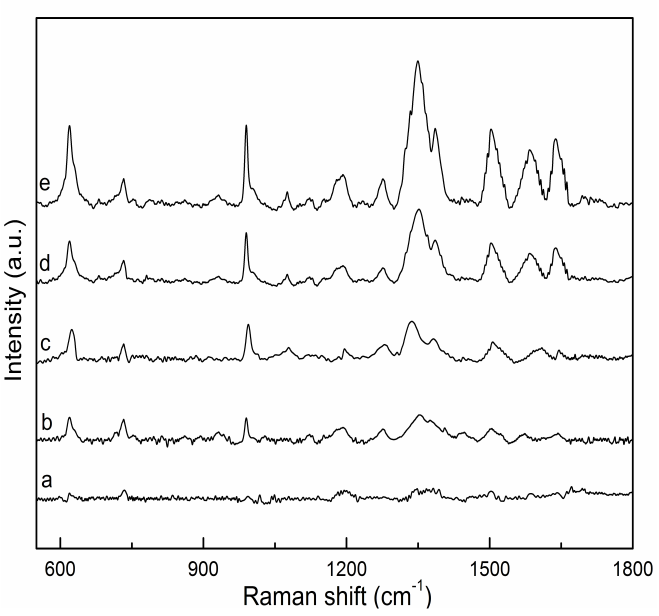
e
d
c
b
a
Intensity (a.u.)
600
900
1200
1500
1800
Raman shift (cm^{-1})

Fig. S7

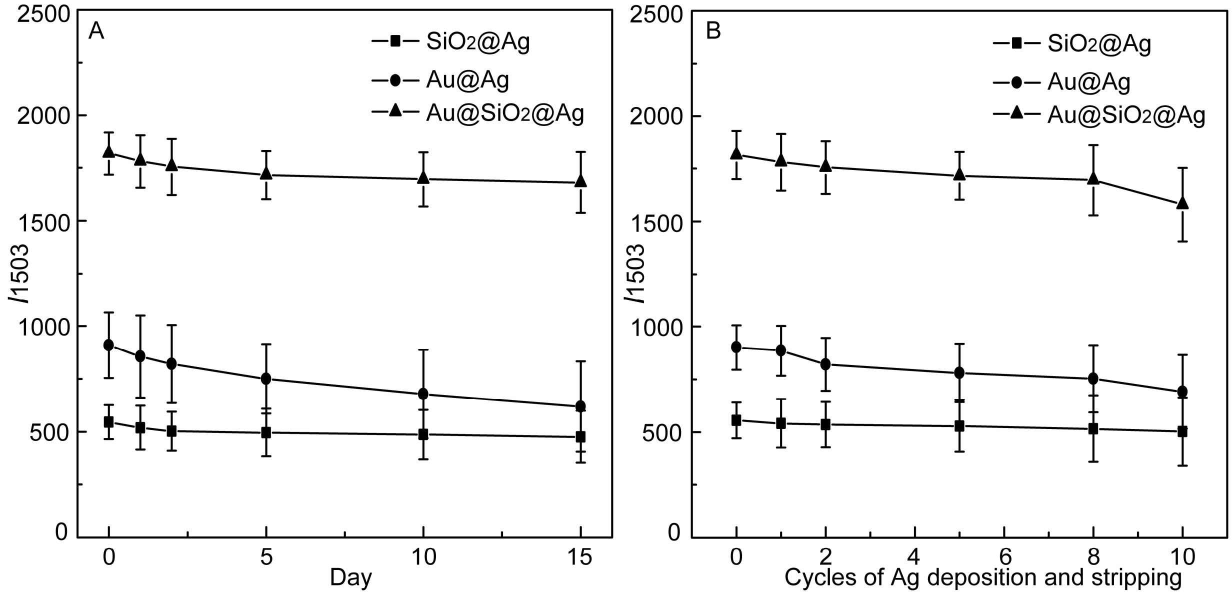
A
B
SiO2@Ag
Au@Ag
Au@SiO2@Ag
I1503
0
500
1000
1500
2000
2500
Day
0
5
10
15
Cycles of Ag deposition and stripping
0
2
4
6
8
10

Fig. S8

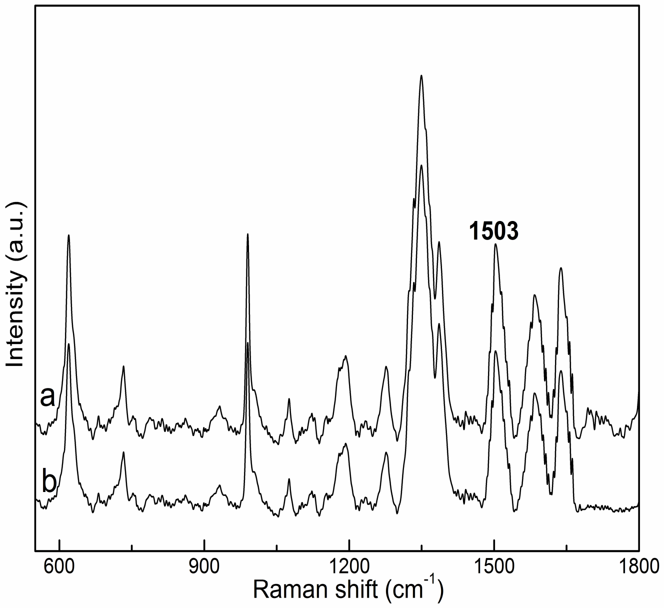
Intensity (a.u.)
1503
a
b
600
900
1200
1500
1800
Raman shift (cm-1)

Fig. S9