Electronic Supplementary Information

Self-Assembled Activated Carbon Nanoparticles for Reliable Time-Discretized Quantitative Surface-Enhanced Raman Spectroscopy

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Preparation of Au colloids and Ag colloids

The synthesis of Au colloids was performed by using the chemical reduction of chloroauric acid with a sodium citrate method. In a typical synthesis, the aqueous solution of HAuCl4 (250 mL, 0.294 mM) was heated to boiling point. Upon boiling, 1.3 mL trisodium citrate (aqueous, 1.0 wt%) was injected quickly to induce particle formation and kept on boiling under stirring vigorously for ca. 30 min. The colloids were cooled at room temperature and the volume is finally adjusted to 250 mL by ultra-pure water for use.

The synthesis of Ag colloids was carried out by using ascorbic acid as reductant and citrate as stabilizer. Typically, a 250 mL aqueous solution containing ascorbic acid (6.0×10^{-4} M) and trisodium citrate (3.0×10^{-3} M) was adjusted to pH=7 by addition of 0.1 M NaOH solution. 2.5 mL of 0.1 M aqueous solution of AgNO3 was added under a stirring speed of 900 rpm in a 30 °C water bath. After 15 min, the reactions were complete. To remove NaOH, the colloids were centrifuged and redispersed into ultra-pure water. Finally, the volume is adjusted to 250 mL by ultra-pure water for use.

Instrumentation

All the Raman measurements were performed with a portable compact laser Raman Spectrometer (BWS415- 785H, B&W Tek). Measurement conditions were the same as main text unless otherwise specified. The cross section of self-assembled activated carbon film was characterized by scanning electron microscope (SEM) (Hitachi SU8010). The Dynamic light Scattering (DLS) was measured by a PALS/90P particle size analyser (Brookhaven, Inc.). The morphology of activated carbon nanoparticles dispersed into DMF was characterized by a transmission electron microscope (TEM) (FEI TEC-NAI G2).

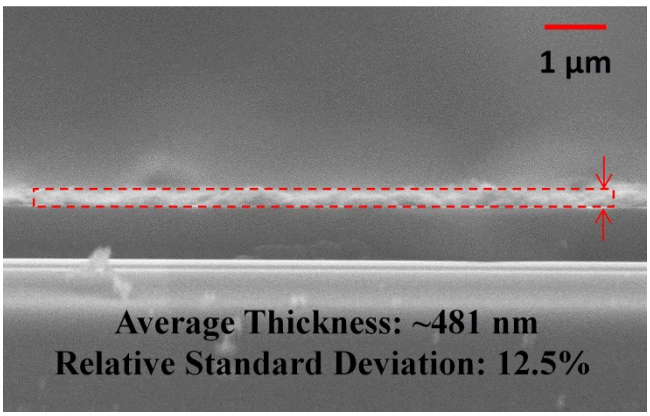

Figure S1. SEM image of cross section of self-assembled activated carbon film. The average thickness is measured by software: Nano Measurer.

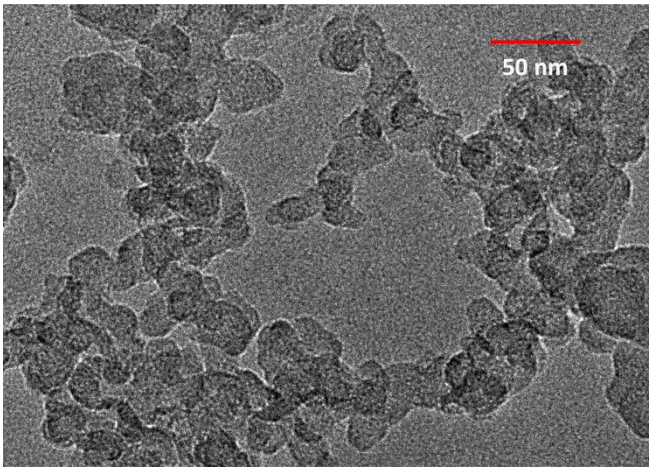

Figure S2. TEM image of activated carbon nanoparticles.

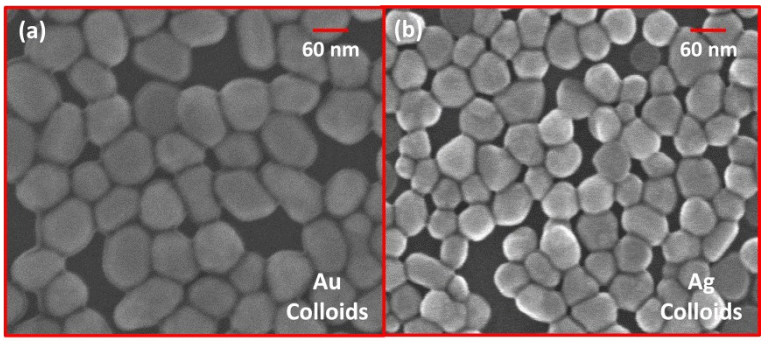

Figure S3. SEM images of Au nanoparticles and Ag nanoparticles. Average Diameters of Au nanoparticles: 86 nm and average Diameters of Ag nanoparticles: 68 nm. The average diameter is measured and calculated by software: Nano Measurer.

Table S1. DLS of activated carbon nanoparticles.

Run NO.	Effective Diameter (nm)	Polydispersity Index
1	231.3	0.127
2	239.5	0.13
3	244.7	0.097
4	241.0	0.14
5	245.7	0.087
6	253.2	0.021
Mean	242.6	0.1

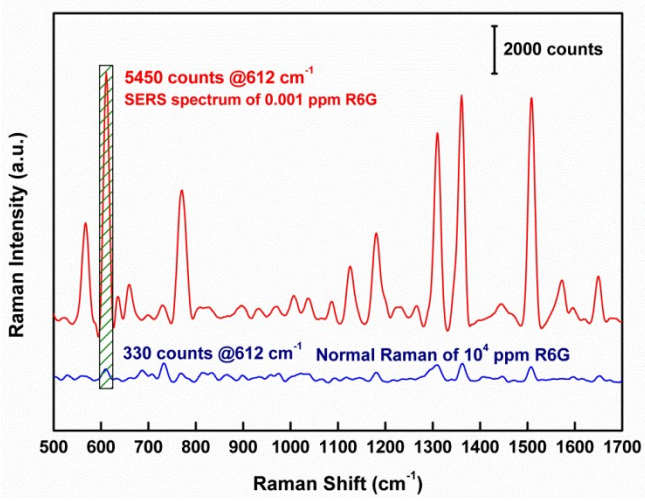

Figure S4. SERS spectra of 0.001 ppm R6G and normal Raman spectra of 10^4 ppm R6G. Excitation wavelength: 785 nm; Excitation intensity: 1.14×10^5; Integration time: 10 s.

Calculation of enhancement factor (EF)

The enhancement performance of SERS substrate is approximately estimated by the calculation of enhancement factor (EF) according to the following equation:[1, 2]

$$EF = (I_{SERS}\times C_0)/(I_0\times C_{SERS}) \quad (1)$$

where, I_{SERS} is the relative intensity of a specific band in the SERS spectra of R6G. I_0 is the relative intensity of the same band in the normal Raman spectra of R6G under the same condition. C_{SERS} is the concentration of adsorbed R6G molecules on an individual particle. C_0 is the concentration of R6G molecules in the excitation volume for normal Raman measurements. The values of these parameters are obtained by SERS measurement of 10^{-3} ppm (~2 nM) R6G and normal Raman measurement of 10^4 ppm (~20 mM) R6G and the results are shown in Figure S1. The enhancement factor of the silver-assisted gold SERS substrate is approximately 1.6×10^8 [EF=(5450/330)$\times10^7$].

Estimation of the ratio expressed in number of particles

Because $HAuCl_4$ and $AgNO_3$ are reduced completely, the ratio of Au/Ag particles can be estimated by the following equations:

$$N_{\text{Ag NP}} = \frac{V_{\text{Ag colloids}}\times C_{\text{Ag-atom}}\times N_A}{\frac{4}{3}\pi r^3_{\text{Ag NP}} / \frac{4}{3}\pi r^3_{\text{Ag-atom}}} \quad (2)$$

$$N_{\text{Au NP}} = \frac{V_{\text{Au colloids}}\times C_{\text{Au-atom}}\times N_A}{\frac{4}{3}\pi r^3_{\text{Au NP}} / \frac{4}{3}\pi r^3_{\text{Au-atom}}} \quad (3)$$

where $V_{\text{Au colloids}}$=85 mL, $V_{\text{Ag colloids}}$=15 mL, $C_{\text{Ag-atom}}$=(2.5 mL×0.1 M)/250 mL=1 mM, $C_{\text{Au-atom}}$=0.294 mM, r AuNP=86 nm, r AgNP=68 nm, r Au-atom= r Ag-atom=1.44 Å. The ratio expressed in number of particles (Au to Ag) calculated is 0.8.

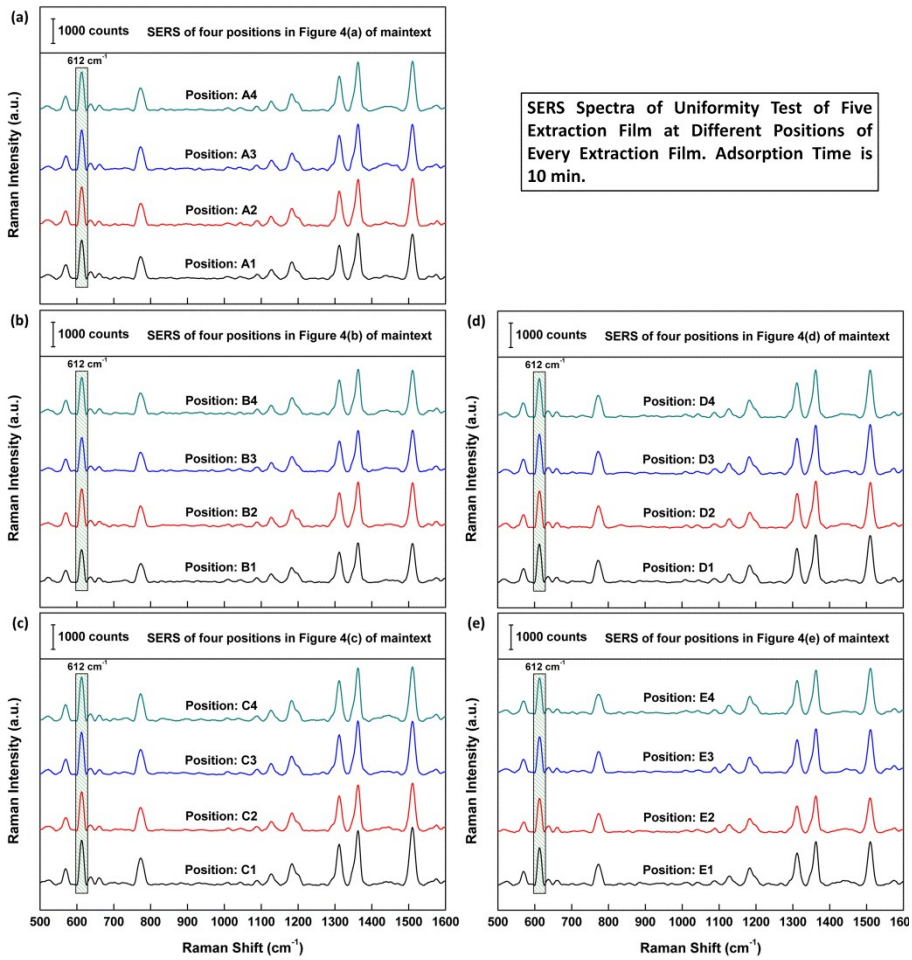

Figure S5. SERS spectra of Figure 4 in maintext.

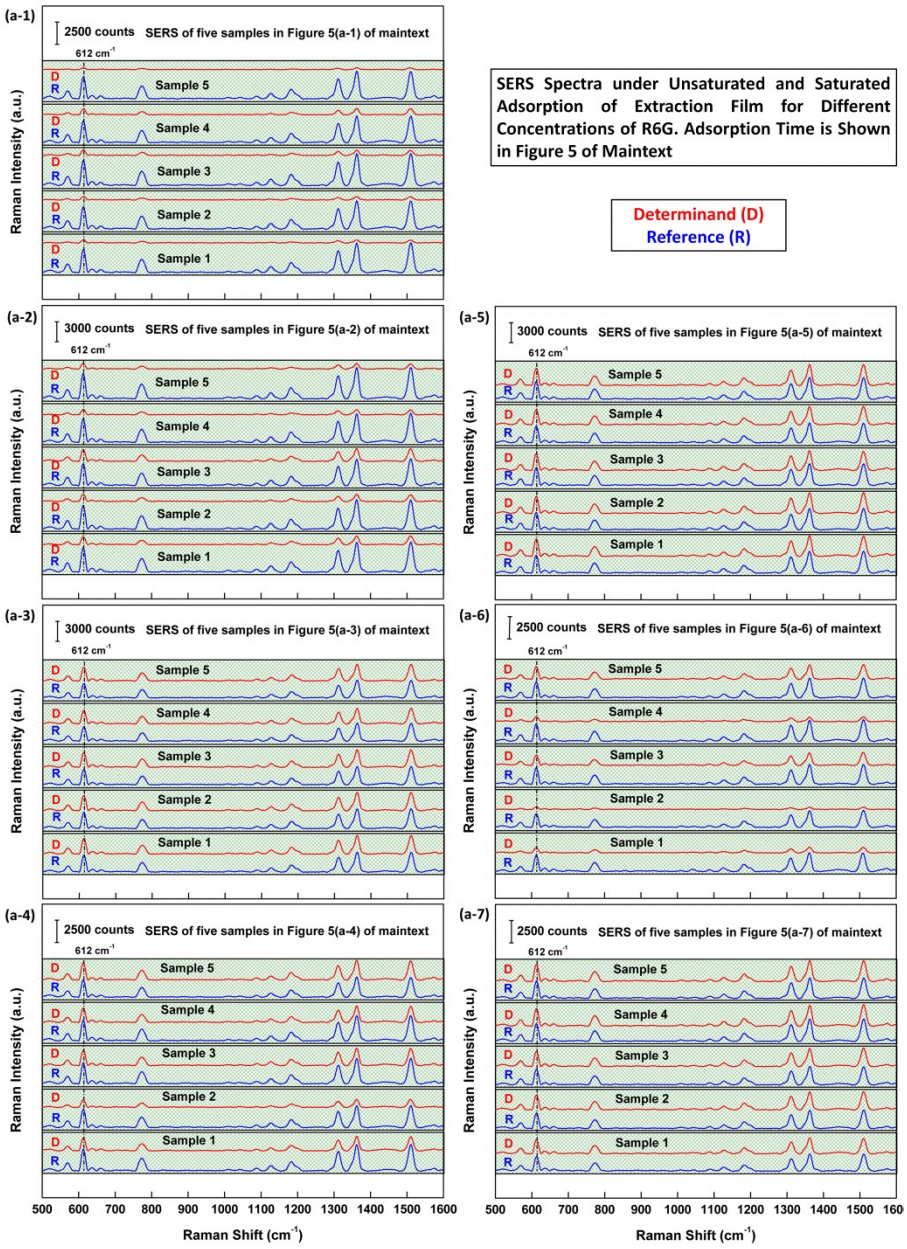

Figure S6. SERS spectra of Figure 5 in maintext.

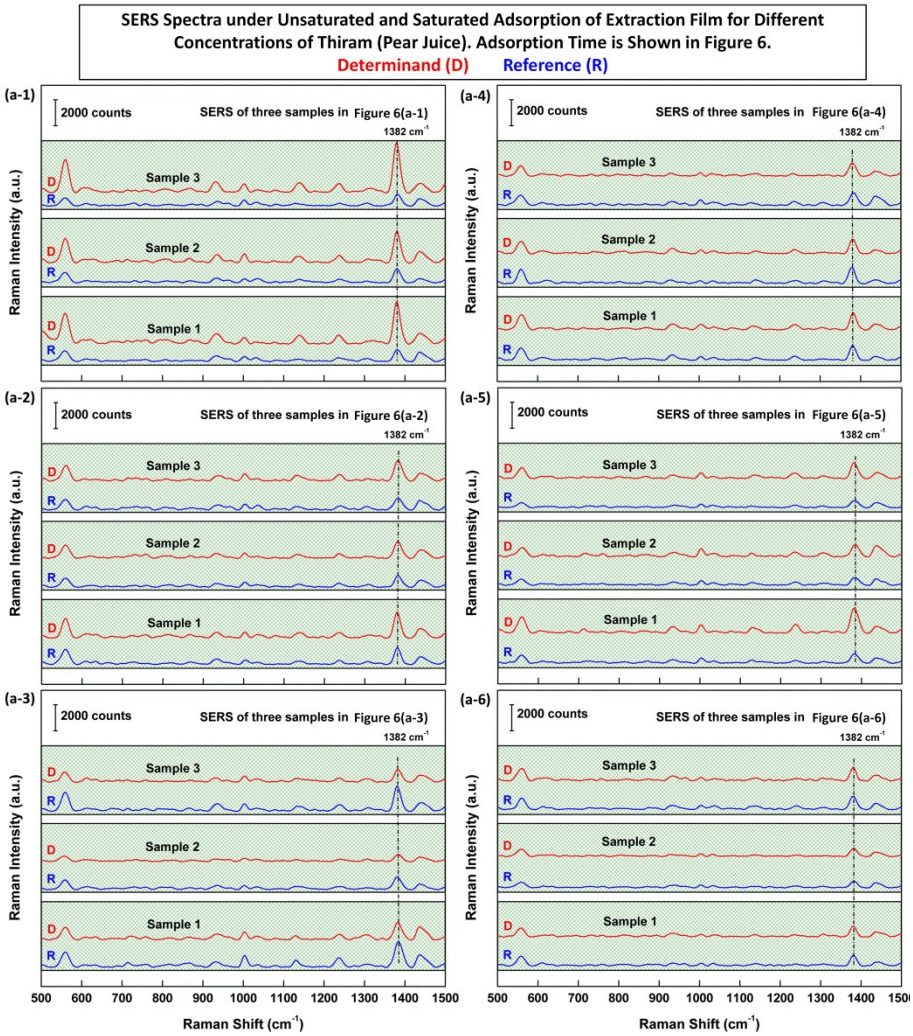

Figure S7. SERS spectra of Figure 6 in maintext.

References

1. X. Zhou, F. Zhou, H. Liu, L. Yang and J. Liu, *Analyst*, 2013, **138**, 5832-5838.
2. E. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, *The Journal of Physical Chemistry C*, 2007, **111**, 13794-13803.