Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Surface confined successive growth of silver nanoplates on a solid substrate with tunable surface plasmon resonances

*Young-Kwan Kim, and Dal-Hee Min**

Supporting figure

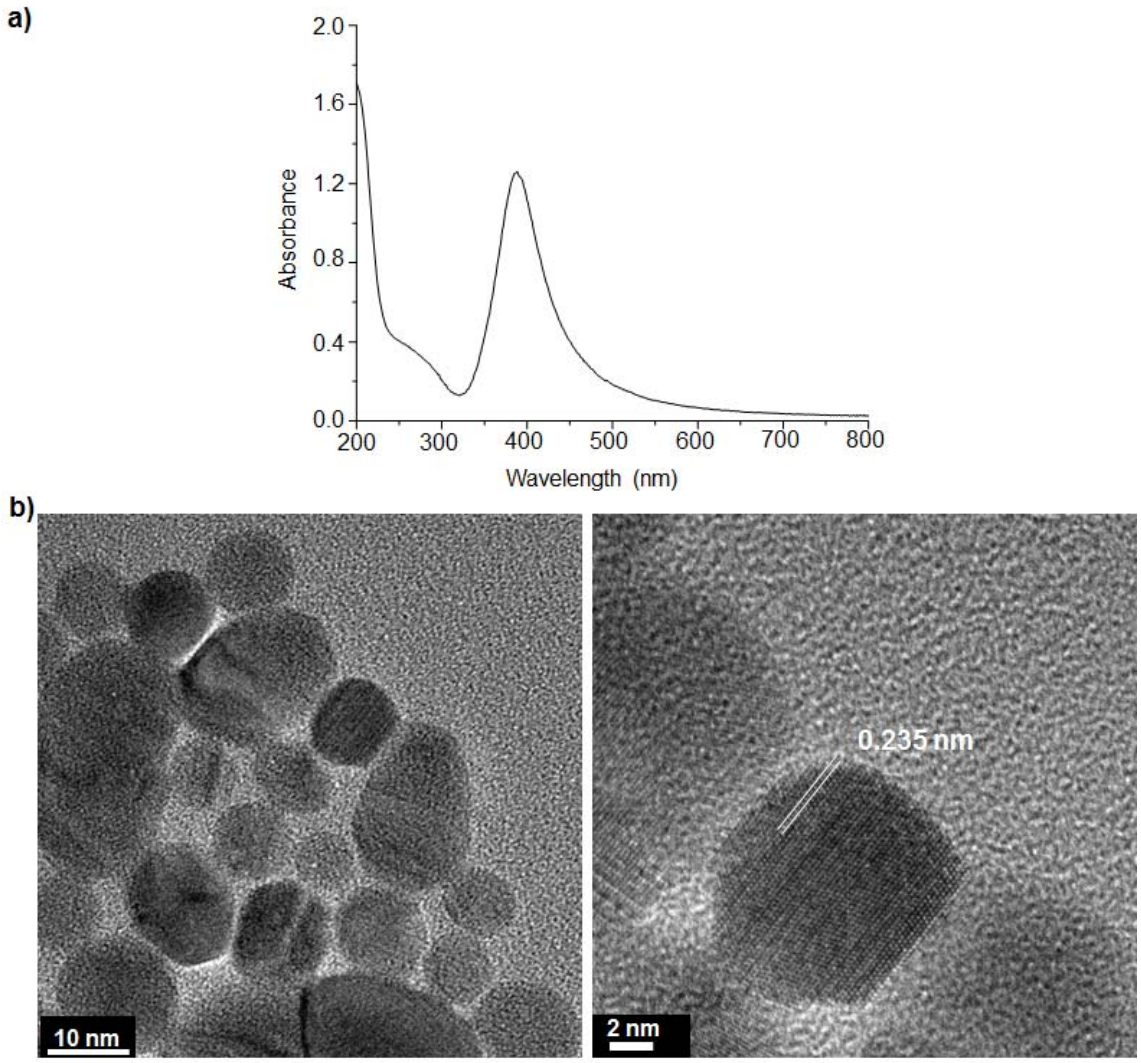

Figure S1. UV-vis spectrum (a) and High resolution transmission electron microscopy (HR-TEM) images of Ag nanoparticles (AgNPs) (b). The synthesized AgNPs showed stacking faults and twin defects with a fringe spacing of 0.235 corresponding to the (111) plane of Ag and used as a seed for direct growth of Ag nanoplates on solid substrates.

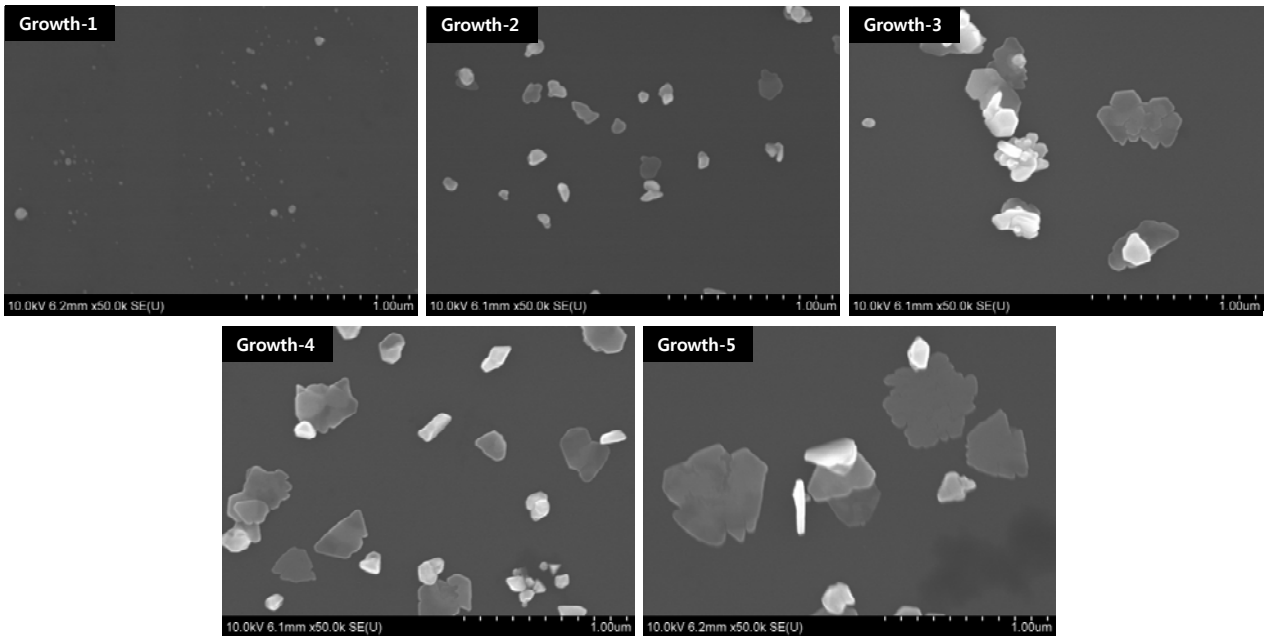

Figure S2. SEM images of PAA-treated Si substrates after control experiment to confirm the role of Ag NPs as seeds for seed-mediated growth. The substrates were applied to our seed-mediated successive growth reaction without surface immobilized AgNPs. As a result, no Ag nanoplate was formed on the PAA-treated Si substrate but there were some large spherical AgNPs (Growth-1). The AgNPs on the substrates might be assembled from the growing solution containing irregular Ag nanostructures formed by self-nucleation in solution phase during this control experiment. It is obvious that self-nucleation is facilitated in this condition compared to our seed-mediated growth condition because there is no seed on solid substrates. Interestingly, the large spherical AgNPs were grown into lateral direction with irregular shape and large size by applying further successive growth cycles. This result indicated that irregularly formed AgNPs could be acted as a growth site for seed-mediated growth but they could not guarantee high density and uniform growth of Ag nanoplates. Therefore, the immobilization of well-synthesized AgNPs on solid substrates is a critical step for successful growth of Ag nanoplates on solid substrates.

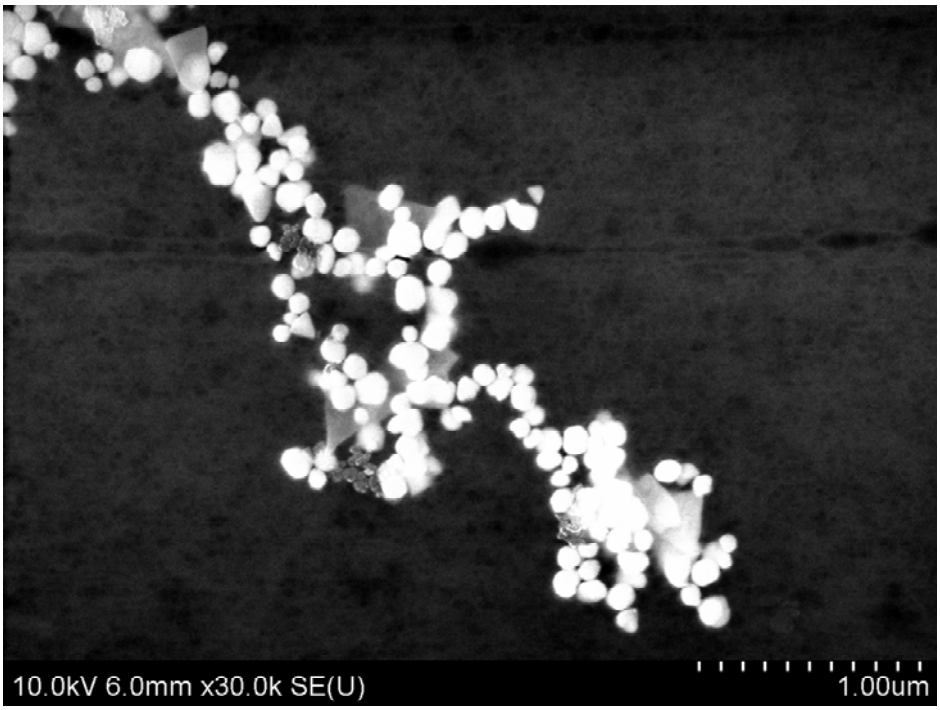

Figure S3. SEM image of Ag nanostructures formed in solution phase during 6 min of seed-mediated growth of Ag nanoplates on solid substrates. The Ag nanostructures were composed of spherical Ag nanoparticles with 130 nm in diameter and triangular nanoplates with 300 – 500 nm in edge length. Those Ag nanostructures were significantly different from the Ag nanoplates formed on solid substrates by seed-mediated growth. Therefore, we have concluded that there was almost no adsorption of Ag nanostructures formed in solution phase during seed-mediated growth experiment.

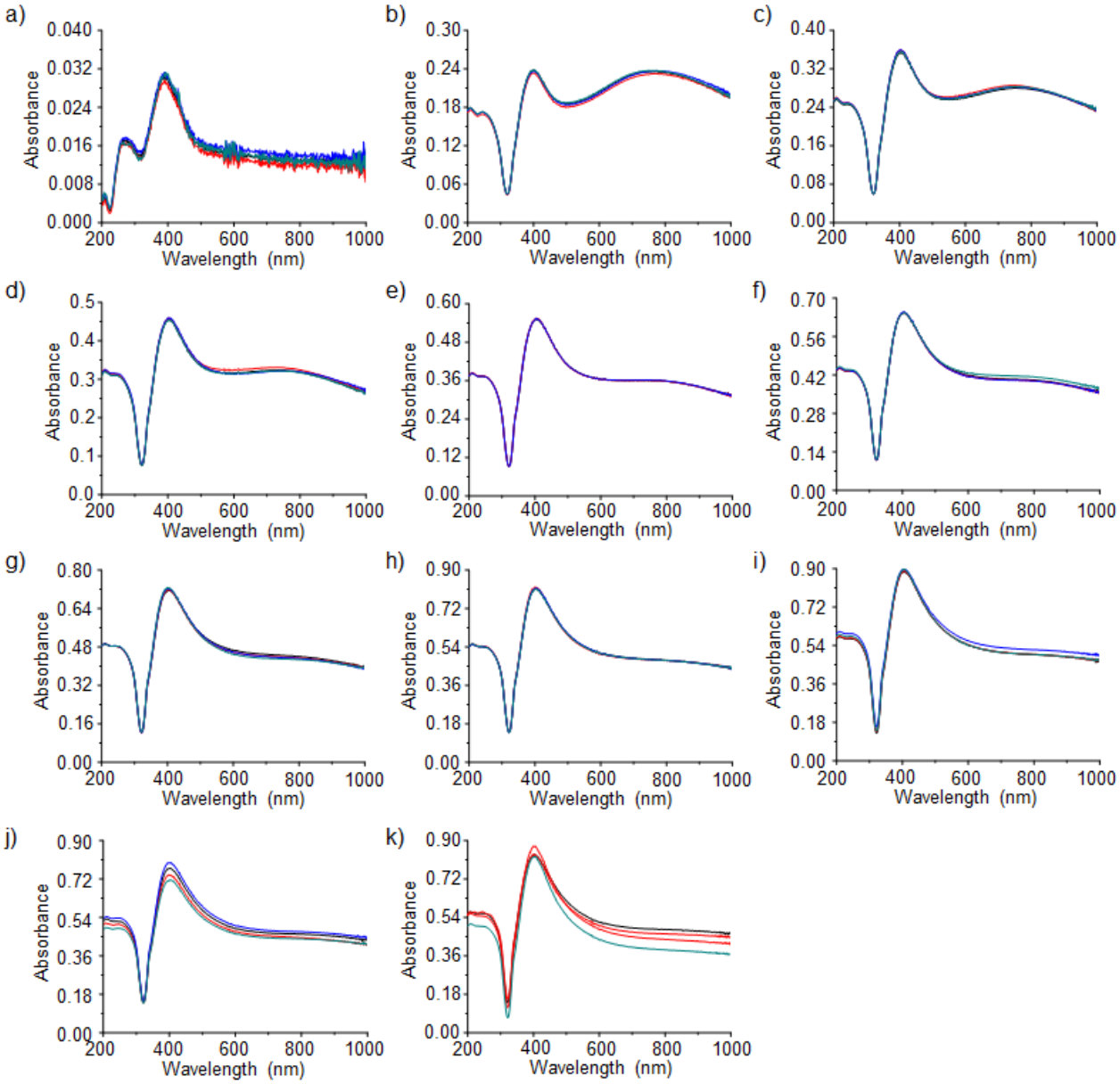

Figure S4. UV-vis-NIR spectra of surface-immobilized AgNP (a) and subsequently grown Ag nanoplates on quartz substrates through 1 – 10 growth cycles (b-k).

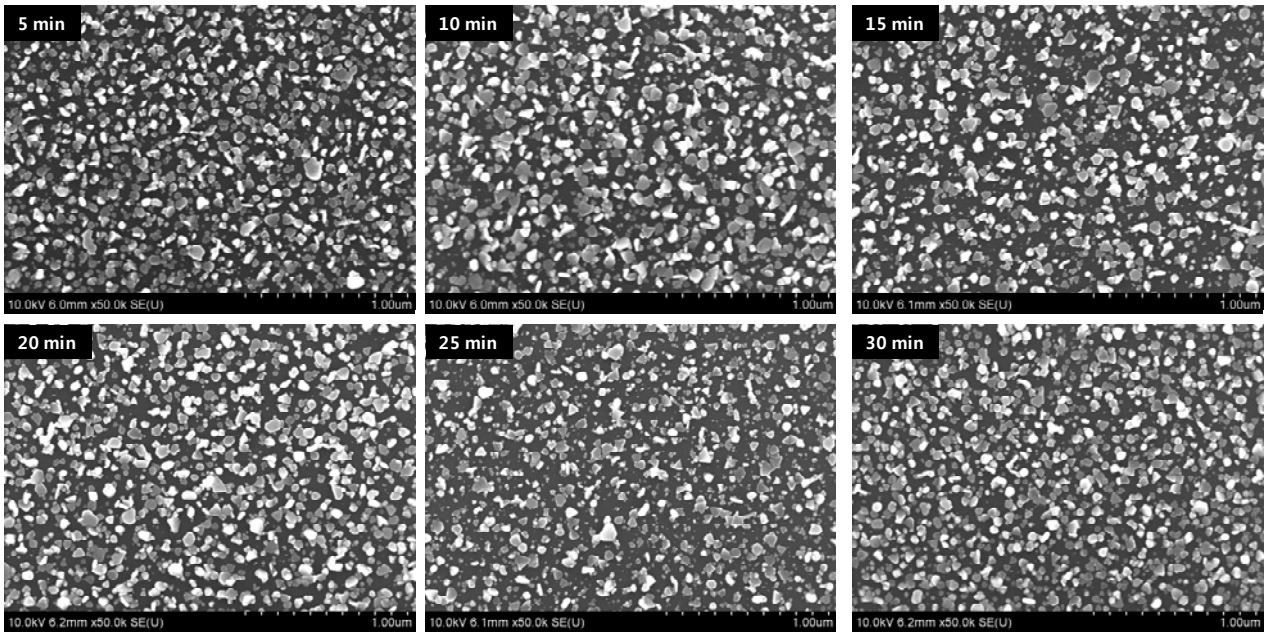

Figure S5. SEM images of Ag nanoplates grown on Si substrates by continuous seed-mediated growth for 5, 10, 15, 20, 25 and 30 min. The size and density of Ag nanoplates were not significantly changed by 30 min growth reaction with feeding of Ag^{+} ion, L-ascorbic acid and sodium citrate at 5 min interval. The results indicated that seed-mediated growth reaction was almost terminated after 5 min by the formation of Ag nanostructures in growth solution induced by self-nucleation.

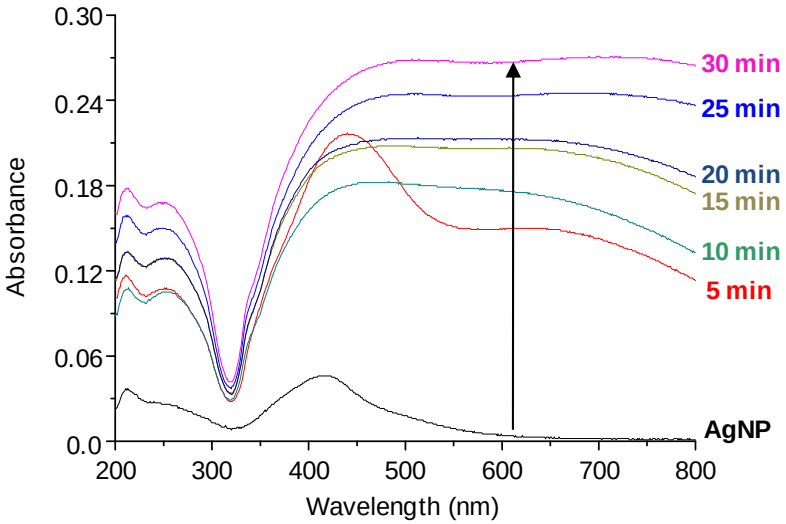

Figure S6. UV-vis spectra of Ag nanoplates grown on quartz substrates by continuous seed-mediated growth for 5, 10, 15, 20, 25 and 30 min. The absorbance at 514 nm corresponding to excitation wavelength of Raman spectroscopy was gradually increased with growth time but the absolute absorbance of 30 min grown Ag nanoplate substrate (0.269) was significantly weak compared to 5 cycle grown Ag nanoplate substrate (0.663). The result showed that Ag nanoplates were slowly grown during continuous growth reaction compared to successive growth reaction. Contrary to SEM data showing no noticeable growth of Ag nanoplates, the slow growth of Ag nanoplates was observed with UV-vis spectroscopy because UV-vis spectroscopy is highly sensitive compared to SEM to characterize density and size of grown Ag nanostructures.

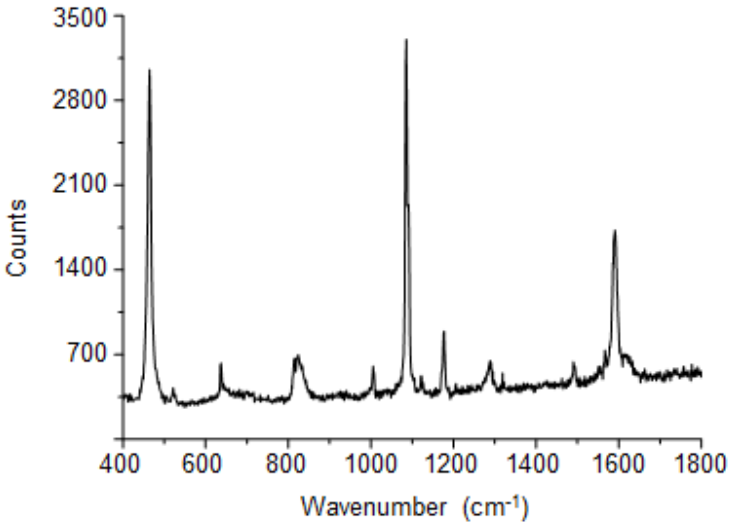

Figure S7. Normal Raman spectrum of 4-aminothiophenol (4-ATP) solid.

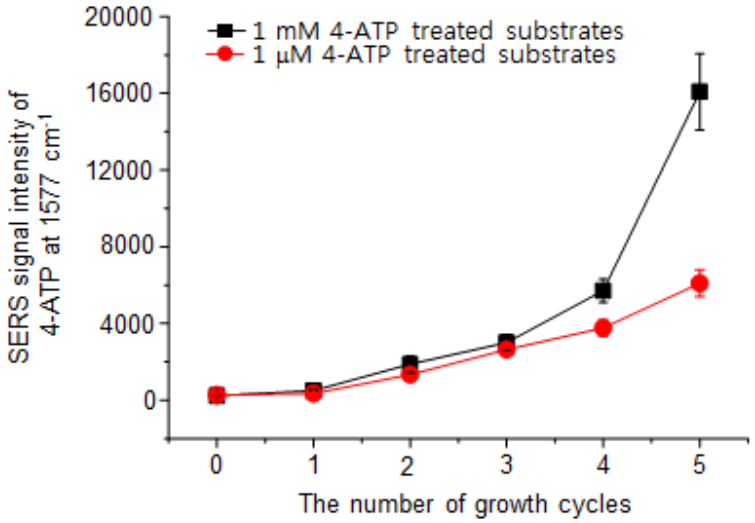

Figure S8. SERS signal intensity of 4-ATP adsorbed on AgNP loaded and Ag nanoplate grown substrates (1-5 growth cycles). AgNP loaded and Ag nanoplate grown substrates with 1 cm^2 size were respectively immersed in 1 mL of 1 μM 4-ATP ethanolic solutions for 24 h, washed with water and ethanol and dried under a stream of nitrogen. The substrates were analyzed by Raman spectroscopy with 514 nm excitation source and the obtained SERS signal intensity of 4-ATP at 1577 cm^{-1} also increased with successive growth cycles. When AgNP loaded and Ag nanoplate grown substrates with 1 cm^2 size were incubated in 1 mL of 1 μM 4-ATP ethanolic solution, all of 4-ATP molecules (about 6×10^{14} molecules per cm^2) were not sufficient to fully cover the surface of substrates because even 1 cm^2 planar surface requires 5×10^{14} 4-ATP molecules for full surface coverage. Therefore, we could obtain approximate value of $N_{surface}$ of 4-ATP on AgNP loaded and Ag nanoplate grown substrates (4.7×10^6).[1] To confirm the insufficient amount of 4-ATP molecules (1 mL of 1 μM) on AgNP loaded and Ag nanoplate grown substrates with 1 cm^2 size (6×10^{14} molecules per cm^2), the all substrates were respectively immersed in 1 mL of 1 mM 4-ATP ethanolic solutions, washed with water and ethanol and dried under a stream of nitrogen. The substrates were analyzed by Raman spectroscopy with 514 nm excitation source and the obtained SERS signal intensity of 4-ATP at 1577 cm^{-1} also increased with successive growth cycles. Based on comparison of 4-ATP SERS signal intensity on AgNP loaded and Ag nanoplate grown substrates treated with different concentration of 4-ATP, all SERS signal intensities of 4-ATP on each substrate increased with increased concentration of 4-ATP and the degree of increase at each growth cycle was enlarged with repeated successive growth cycles. This result clearly indicated that the surface of AgNP loaded and Ag nanoplate grown substrates were not fully covered with 4-ATP after incubation in 1 μM ethanolic solution of 4-ATP for 24 h and the obtained EF values of each substrate were obviously under-estimated with successive growth cycles. Each data point of SERS signal intensities at 1577 cm^{-1} was average value with standard deviation obtained at five different points on each substrate.

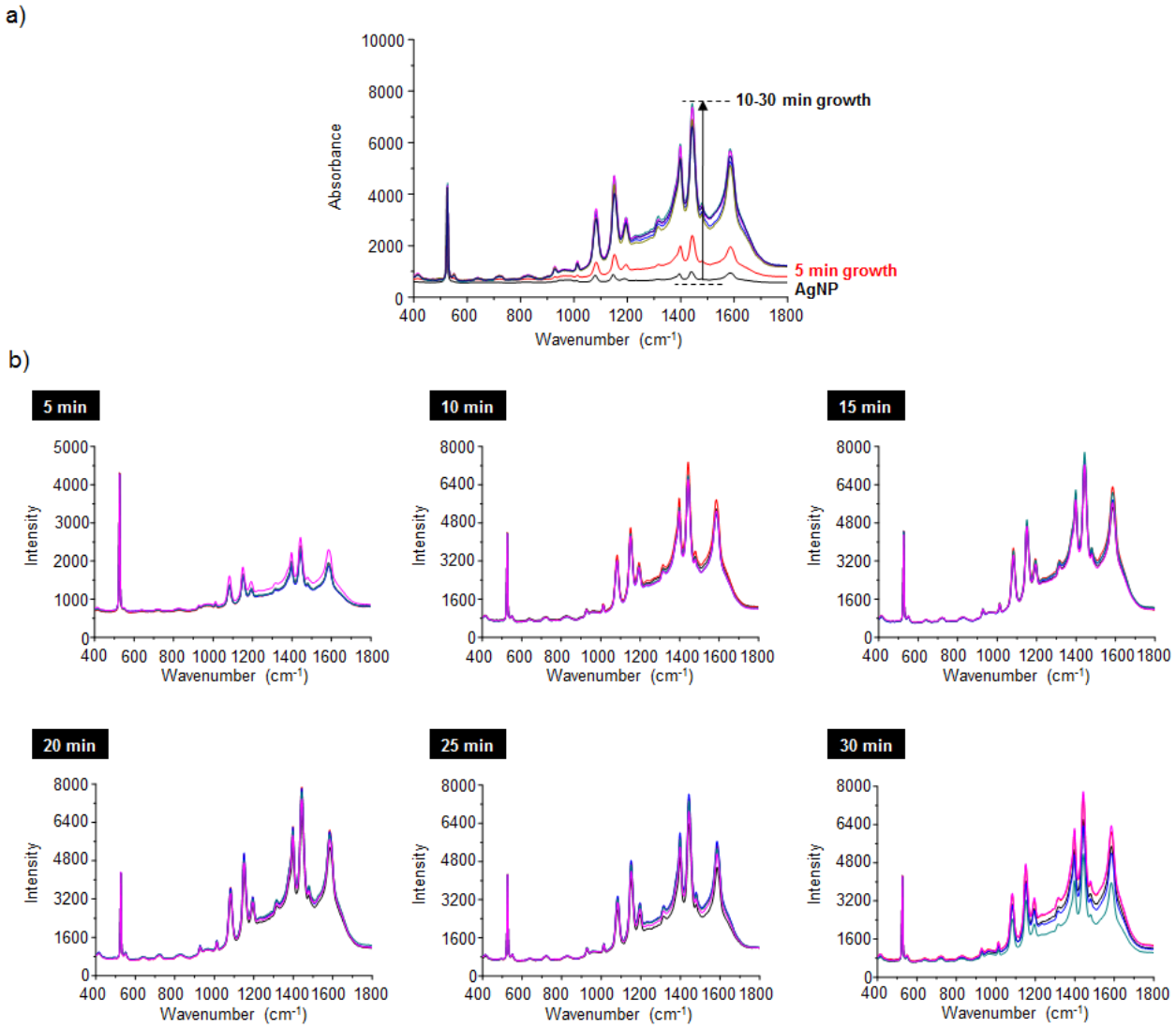

Figure S9. a) SERS spectra of 4-ATP on surface-immobilized AgNP and subsequently grown Ag nanoplates on Si substrates by continuous seed-mediated growth for 5, 10, 15, 20, 25, 30 min growth reaction time. The SERS signal of 4-ATP was gradually enhanced by 5 and 10 min growth reaction but the enhancement was almost halted after 10 min. This result well concurred with SEM (Figure S4) and UV-vis (Figure S6) analysis data. b) SERS spectra of 4-ATP were obtained at five points on each continuously grown Ag nanoplate substrates and each 4-ATP SERS graph showed reproducible and stable intensity.

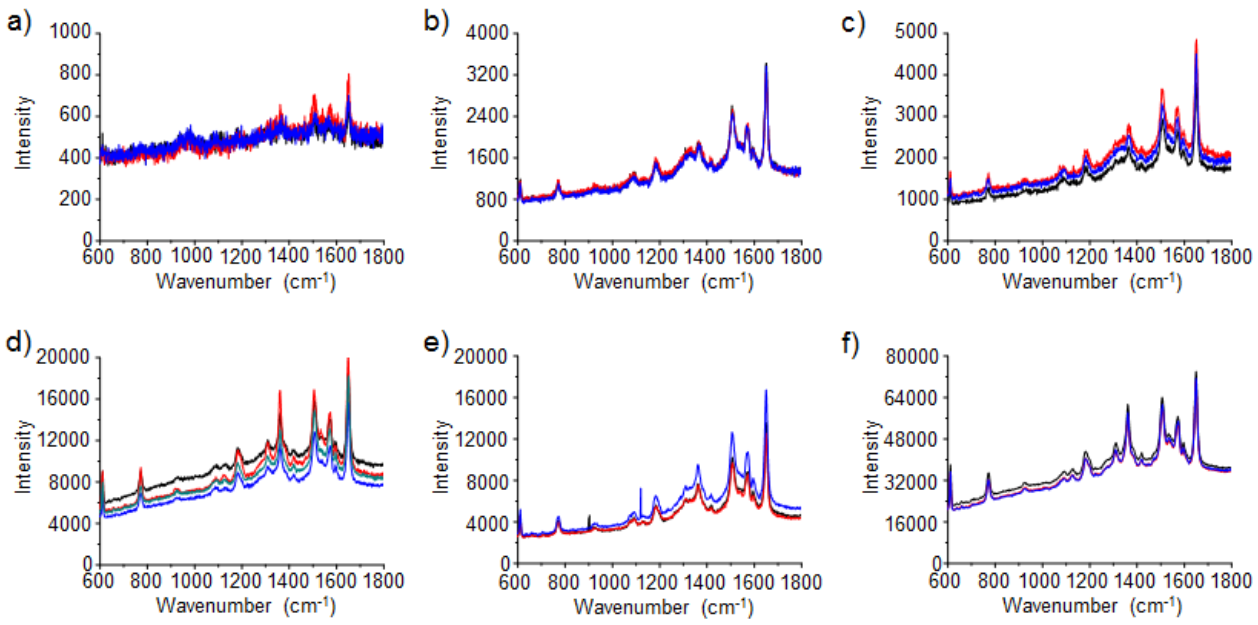

Figure S10. SERS spectra of R6G obtained on the surface-immobilized AgNP (a) and on the subsequently grown Ag nanoplates on Si substrates through 1 – 5 growth cycles (b-f) obtained with 514 nm excitation source. The substrates were respectively incubated in 1×10^{-4} M aqueous solution of R6G for 12 h.

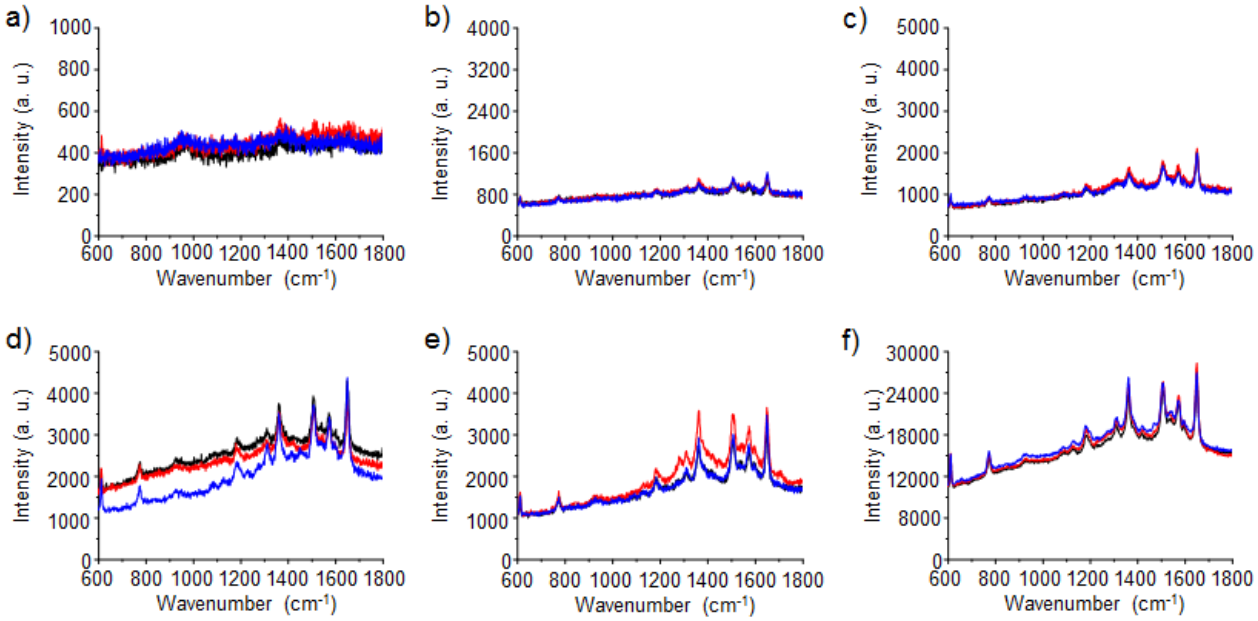

Figure S11. SERS spectra of R6G obtained on the surface-immobilized AgNP (a) and on the subsequently grown Ag nanoplates on Si substrates through 1 – 5 growth cycles (b-f) obtained with 514 nm excitation source. The substrates were respectively incubated in 1×10^{-5} M aqueous solution of R6G for 12 h.

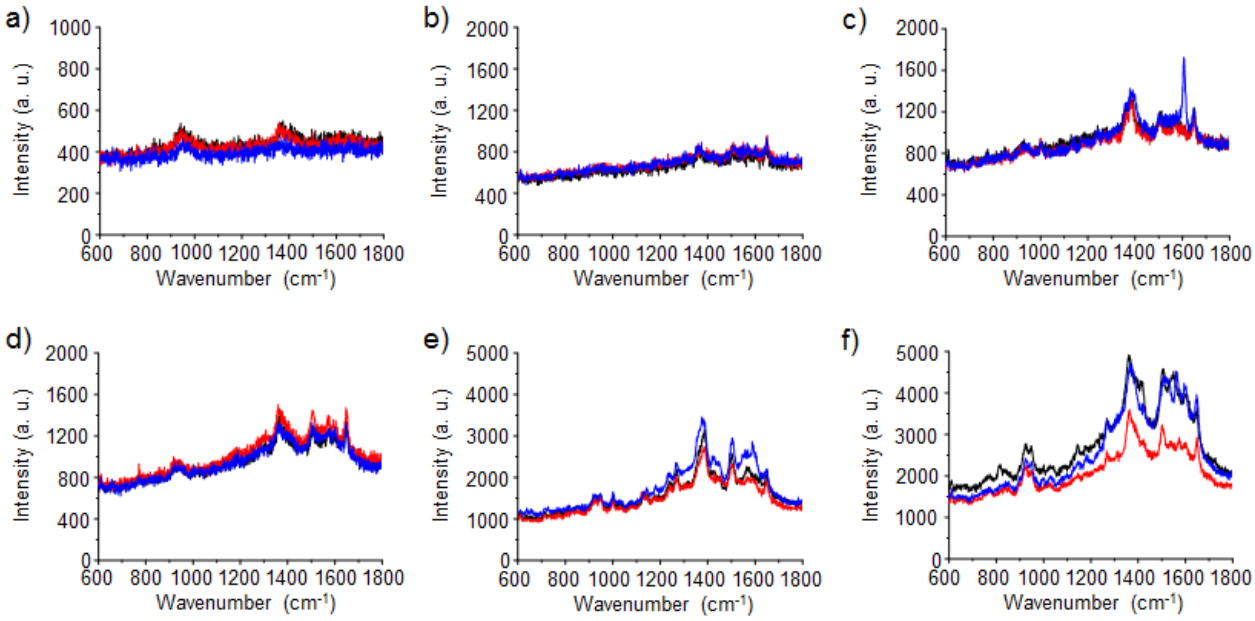

Figure S12. SERS spectra of R6G obtained on the surface-immobilized AgNP (a) and on the subsequently grown Ag nanoplates on Si substrates through 1 – 5 growth cycles (b-f) obtained with 514 nm excitation source. The substrates were respectively incubated in 1×10^{-6} M aqueous solution of R6G for 12 h.

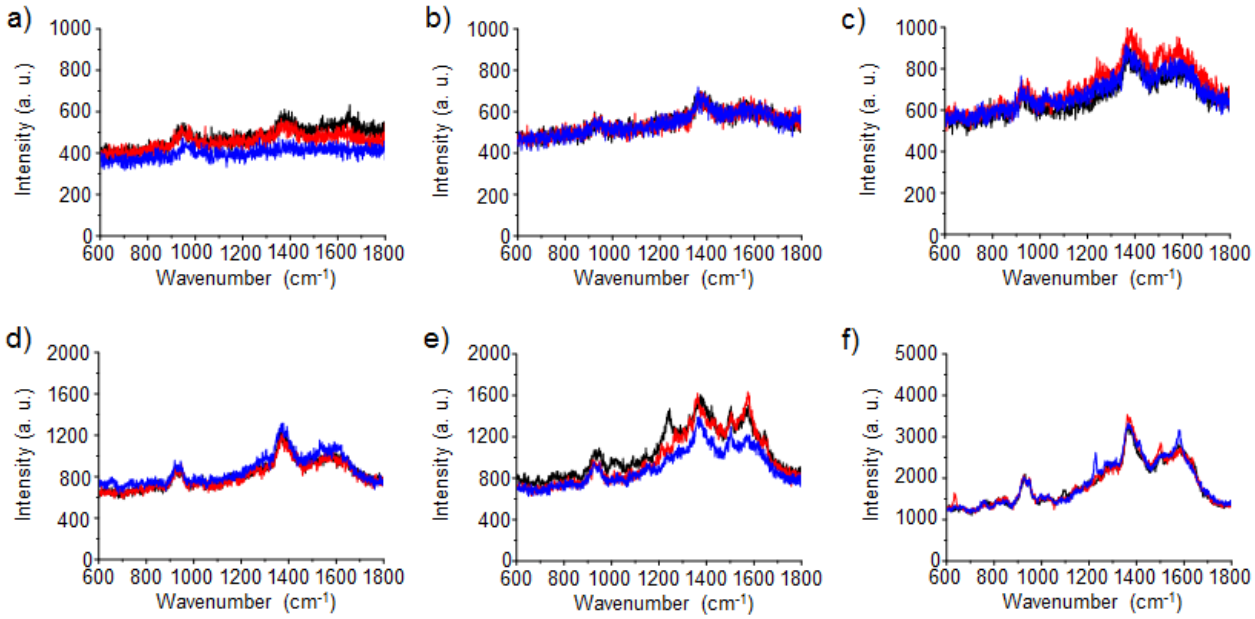

Figure S13. SERS spectra of R6G obtained on the surface-immobilized AgNP (a) and on the subsequently grown Ag nanoplates on Si substrates through 1 – 5 growth cycles (b-f) obtained with 514 nm excitation source. The substrates were respectively incubated in 1×10^{-7} M aqueous solution of R6G for 12 h.

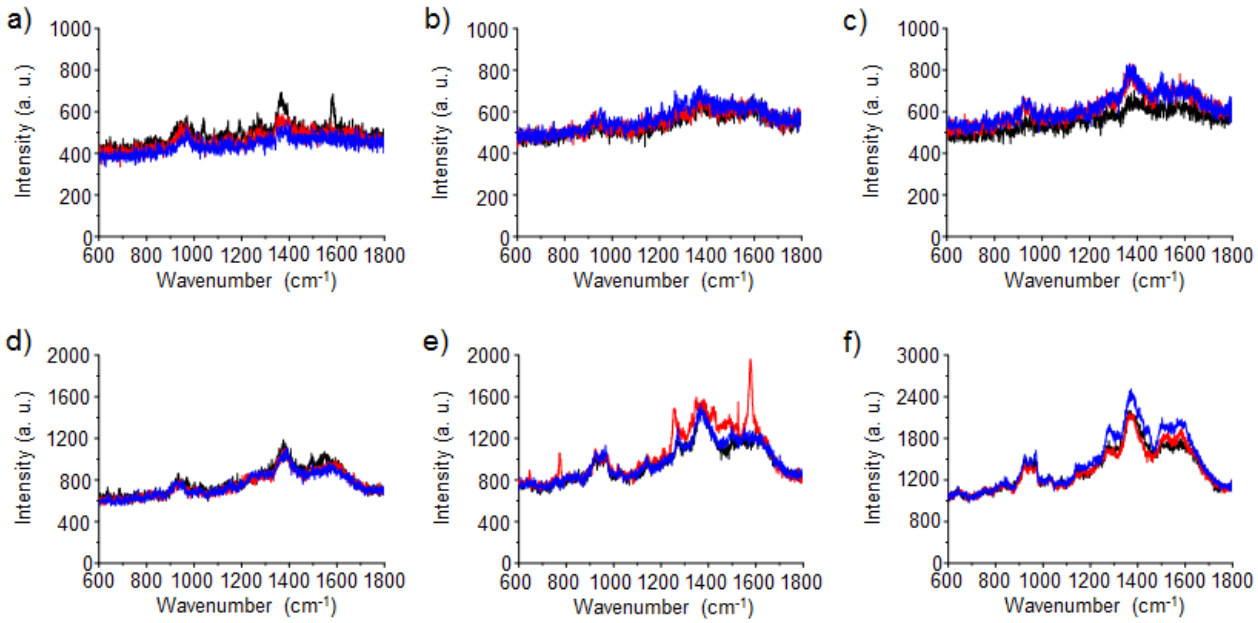

Figure S14. SERS spectra of R6G obtained on the surface-immobilized AgNP (a) and on the subsequently grown Ag nanoplates on Si substrates through 1 – 5 growth cycles (b-f) obtained with 514 nm excitation source. The substrates were respectively incubated in 1×10^{-8} M aqueous solution of R6G for 12 h.

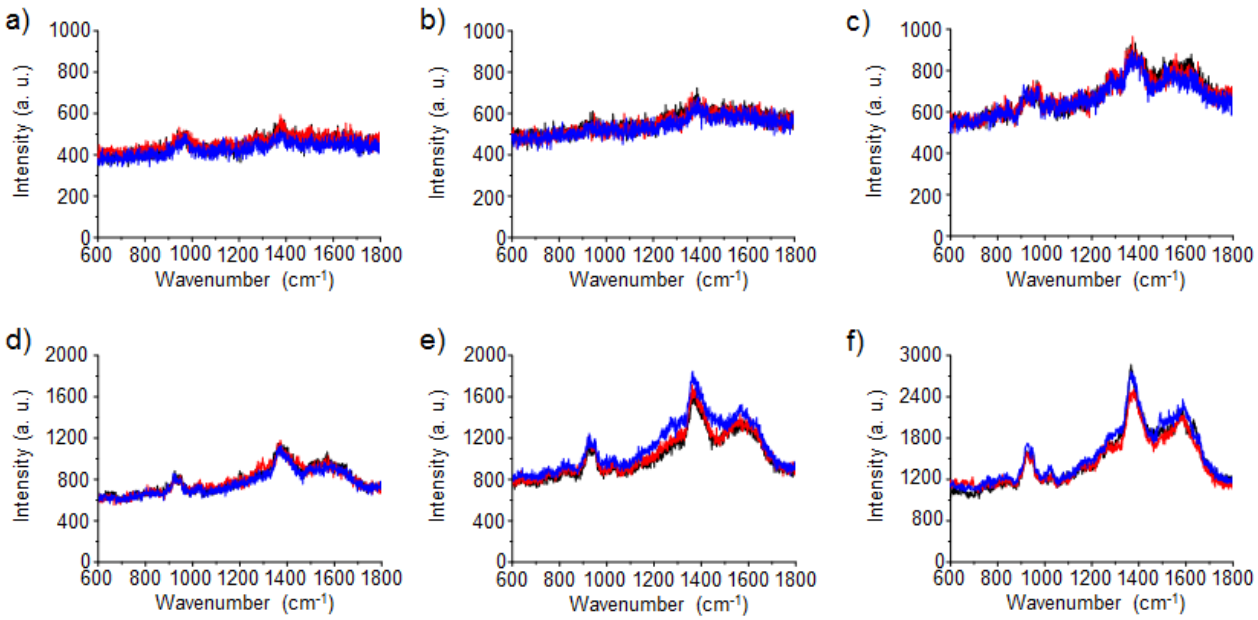

Figure S15. SERS spectra of R6G obtained on the surface-immobilized AgNP (a) and on the subsequently grown Ag nanoplates on Si substrates through 1 – 5 growth cycles (b-f) obtained with 514 nm excitation source. The substrates were respectively incubated in 1×10^{-9} M aqueous solution of R6G for 12 h.

Supporting reference

1. G. Liu, W. Cai, L. Kong, G. Duan, F. Lü, *J. Mater. Chem.*, 2010, **20**, 767.