Supporting Information

**pH-Tunable Plasmonic Properties of Ag Nanoparticle Cores in Block Copolymer Micelle Arrays on Ag films**

Jiwon Lee,‡ Seugmin Yoo,‡ Myoungsoo Shin, Ayoung Choe, Soojin Park,* and Hyunhyub Ko*

J. Lee, S. Yoo, M. Shin, A. Choe, Prof. S. Park, Prof. H. Ko
Department of Energy Engineering, School of Energy and Chemical Engineering
Ulsan National Institute of Science and Technology (UNIST)
UNIST-gil 50, Ulsan, 689-798, Republic of Korea

*E-mail: spark@unist.ac.kr, hyunhko@unist.ac.kr

‡These authors contributed equally.

**Figure S1.** TEM images of S4VP@Ag monolayer micellar film with relatively small P4VP block ratio at (a) pH = 2, (b) as-prepared (pH = 7), and (c) pH = 10.
Figure S2. (a) Thickness and (b) surface roughness variation of S4VP@Ag films were measured by AFM at various pH conditions. The pH was increased from 2 to 10. AFM images of S4VP@Ag film of (c) as-prepared sample and treated in (d) pH = 8. In a specific condition (pH = 8, regarded as transition point occurring surface reconstruction in basic conditions), film thickness was increased while surface roughness decreased without surface reconstruction, implying that S4VP@Ag micellar films were swollen with increasing gap between Ag NPs and Ag film.
Figure S3. Cross-sectional line profile of S4VP@Ag monolayer film on Si substrate at pH = 10. Cross-sectional line profile was obtained from white dotted line in left AFM image, indicating small pores in the center of each micelle.
Figure S4. UV-vis absorption spectra of as-prepared S4VP micelles on Ag film for comparison of (a) before and (b) after reduction. The localized surface plasmon of Ag NP shows at 430 nm wavelength with S4VP resonance peak.
Figure S5. Dark-field microscopy images of S4VP@Ag monolayer film on Si substrate at (a) pH = 2, (b) as-prepared (pH = 7), and (c) pH = 10.
Figure S6. AFM images of S4VP@Ag monolayer film on Ag substrate at (a) pH = 2, (b) as-prepared (pH = 7), and (c) pH = 10. (d) These surface density of S4VP@Ag on Ag and Si substrates are plotted by bar graph based on AFM images. All surface morphologies in different pH conditions are almost same for Si substrate.
Figure S7. Raman intensity plots for S4VP@Ag monolayer films fabricated by (a) S4VP (31k) and (b) S2VP (265k) without BT target molecule. A ring stretching mode (1602 cm⁻¹) of a P4VP block was plotted, instead of characteristic wavelength of benzenethiol (BT) molecules.