pH-Tunable Particle-Film Gap-Plasmons of Ag Nanoparticle Cores in Block Copolymer Micelles Arrays on Ag Films

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Recently, plasmonic systems based on metal nanoparticles on a metal film have generated great interest for ultra-sensitive surface-enhanced Raman spectroscopy (SERS) as bio/chemical sensors. Particle-on-film plasmonic systems provide unique hybridizing plasmon modes caused by coupling of localized surface plasmons (LSPs) and propagating surface plasmons (PSPs), which is significantly improved plasmonic effects compared to those of interparticle plasmonic systems. Here, we suggest a particle-film plasmonic system with active control of particle-film gap distances based on pH-responsive block copolymer micelle-metal monolayer arrays on metal films. We characterized reconstruction of PS-b-P4VP films and relative position of Ag nanoparticles (Ag NPs) inside the micellar monolayer films under various conditions by UV-vis, TEM, AFM, and XPS. In particular, at high pH values (pH = 10), the strongest SERS intensity was detected due to the high E-fields at the decreased gap of the Ag NP-Ag film. Finally, we demonstrate that the pH-sensitive polymer micelles modulate gap distances between Ag NPs within micelles cores and Ag films, leading to great changes in particle-film plasmon couplings that strongly influence the SERS signal.