Self-Assembled SERS Substrate with High Sensitivity and Excellent Reproducibility

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We introduce a simple but robust method to fabricate an ultrahigh density array of silver nanocluster for surface enhanced Raman spectroscopy (SERS) substrate with high sensitivity and excellent reproducibility at a very large area (wafer scale). For this purpose, poly(4-vinyl pyridine) (P4VP) micelles were prepared by spin coating of polystyrene-*block*-P4VP copolymer (PS-*b*-P4VP) with various block ratios of PS and P4VP in toluene/tetrahydrofuran solution on a silicon substrate. After silver nitrates were incorporated into the micelle cores followed by the reduction to silver nanoclusters, we systematically controlled the gap distance between two neighboring silver nanoclusters ranging from 8 to 61 nm, while the diameter of each silver nanocluster was kept nearly constant (~ 25 nm). Fabricated SERS substrate with a gap distance of 8 nm showed very high signal intensity with a maximum SERS enhancement factor as high as 10^8, which is enough to detect a single molecule, and excellent reproducibility (less than ± 5%) of the signal intensity. This is because of uniform size and gap distance of silver nanoclusters in a large area.