Nanoimprinted-Block Copolymer-Based Porous Nanocone Substrate for SERS Enhancement

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Abstract: Raman spectroscopy is one of the most powerful techniques for chemical detection, but the low sensitivity originated from the extremely small cross-section of the Raman scattering limits the practical use of Raman spectroscopy. To overcome this problem, Surface Enhanced Raman Scattering (SERS) has been intensively studied for several decades. Because the SERS effect is mainly induced from strong electromagnetic near-field enhancement as a result of localized surface plasmon resonance of metallic nanostructures, it is important to design the plasmonic structures with high density of electromagnetic hot spots for SERS substrate. One of the useful fabrication methods is using porous nanomaterial as a template for metallic structure. Internal pores on a scale of tens of nanometers can be strong EM hotspots by confining the incident light. Also, porous structures can capture more target molecules than non-porous structures in a same detection spot thanks to the large surface area. Herein we report the facile fabrication method of porous SERS substrate by integrating solvent-assisted nanoimprint lithography and selective etching of block copolymer. We obtained nanostructures with high porosity via simple selective etching of the one microdomain of the diblock copolymer. Furthermore, we imprinted of the nanocone patterns into the spin-coated flat block copolymer film to make three-dimensional SERS substrate for the high density of SERS hot spots as well as large surface area. We used solvent-assisted nanoimprint lithography (SAIL) to reduce the fabrication time and cost for patterning BCP film by taking advantage of a solvent which dissolves both polystyrenre and poly(methyl methacrylate) domain of the block copolymer, and thus block copolymer film was molded under the low temperature and atmospheric pressure in a short time. After Ag deposition, we measured Raman intensity of dye molecules adsorbed on the fabricated structure. Compared to the Raman signals of Ag coated solid nanocone, porous nanocone showed 10 times higher Raman intensity at 1510 cm(-1) band. In conclusion, we fabricated porous metallic nanocone arrays with high density electromagnetic hotspots by templating nanoimprinted diblock copolymer with selective etching and demonstrated its capability as an effective SERS substrate.

Keywords: block copolymer, porous nanostructure, solvent-assisted nanoimprint, surface-enhanced Raman spectroscopy

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