

Engineering for Ultra-Rough Surface of Polystyrene Microspheres through RIE Technique and Application in SERS

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Experimental section

1. Chemicals and Materials. The 5 % aqueous suspensions of PS spheres with diameter of 3.5 μm were purchased from Shanghai Hugebio Corporation. Acetone (>99.5%) was purchased from Yantai Far East Fine Chemicals Corporation. Absolute ethanol (>99.7%) was purchased from Tianjin Fuyu Fine Chemicals Corporation. 4-Aminothiophenol (>98%) was purchased from Shanghai Aladdin Biochemical Technology Corporation. All these chemicals and solvents were used without further purification. Deionized water (18.2M Ω ·cm in resistivity, Barnstead Easy Pure II 7138) was used for all experiments.

2. Pretreatment of substrates. We first performed ultrasonic cleaning using acetone, absolute ethanol, and deionized water, each for a duration of 5 minutes. After cleaning, the wafers were dried in vacuum.

3. Preparation of monolayer PS colloidal spheres. Initially, we prepared an appropriate amount of PS/absolute ethanol suspension in a ratio of 1:1. To remove any residual PS aggregates, the suspension underwent ultrasonic cleaning for 2 minutes. Subsequently, using a pipette gun, the suspension was slowly injected into the edge of the germanium sheet, which was covered with an appropriate amount of deionized water. In order to balance the tension difference at the interface, the microspheres spontaneously formed a layer of hexagonal close-packed structure on the liquid surface, remaining stationary and awaiting the natural evaporation of water. This process resulted in the desired germanium sheet covered with a single-layer of PS microspheres.

4. Reactive ion etching parameters. The reactive ion etching machine (RIE-100) used in the etching stage is manufactured by Beijing Zhongke Tailong Electronic Technology Corporation. To minimize interference when probing the effect of C atomic concentration on etching, we maintain a consistent concentration of F atoms, we set the O₂ flux to 30 sccm, controlled the fluxes of SF₆ and CHF₃ gases at 40 sccm and 80 sccm respectively, and set the etching power and time for both to 60 W and 600 seconds.

5. Simulation of pressure distribution on the surface of PS microspheres. We have simulated the pressure distribution on the surface of PS microsphere, and since we only need to obtain the differential distribution of impact pressures at different locations of the spherical surface subjected to polarized ions, we have carried out appropriate idealization in setting the detailed parameters. In this case, we set the polarized ions in the space to be S and F ions, and their spatial distribution density is set to fill the entire space in order to ensure that the entire upper hemisphere can be impacted and thus

output a continuous spherical red-blue heat map. The direction of motion of the ions was from top to bottom, and the inlet and outlet velocities were both set to 1000 m/s. When PS microsphere was introduced into the model, we set the integration space large enough to ensure the accuracy of the simulation results.

6. Measurement of SERS spectra. The manufacturer of the micro-area laser Raman spectrometer (Finder One) used to test the SERS spectra is Beijing Zolix Instruments Corporation. The magnetron sputtering machine (VTC-16-SM) and Ag target used for sputtering the Ag layer were purchased from Hefei Kejing Material Technology Corporation. We used the magnetron sputtering machine to sputter a 20s Ag layer (10nm thickness) on each three substrates. Then, we configured a 4-ATP ethanol solution with a concentration of 10^{-4} M and the Ag-coated substrates were immersed in it for 6h and then taken out, each substrate was rinsed separately in flowing anhydrous ethanol for 1 min continuously to remove excess 4-ATP molecules. The Raman spectrum was measured after the substrates were dried in a vacuum drying oven. Where the tested laser wavelength is 785 nm, and the integration time is set to 10 seconds. We performed 10 times SERS test on each substrate immersed in 4-ATP solutions, the test is considered successful when the intensity of the 1075 cm^{-1} characteristic peak is greater than or equal to three times the intensity of the background signal in this location six or more times. The concentration at the time of the previous test at which we judged the test to have failed was the detection limit. We selected the data with the median intensity of the 1075 cm^{-1} characteristic peak as the detection result from all the conforming detections for each substrate.

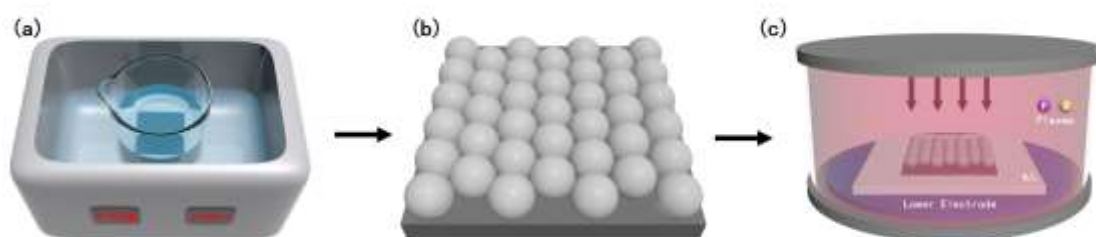


Figure S1. (a) Pretreatment of germanium wafers; (b) Ge sheet covered with a single layer of PS sphere thin film obtained by gas-liquid interfacial self-assembly method; (c) The obtained substrate is etched in a reactive ion etching machine with different gases.

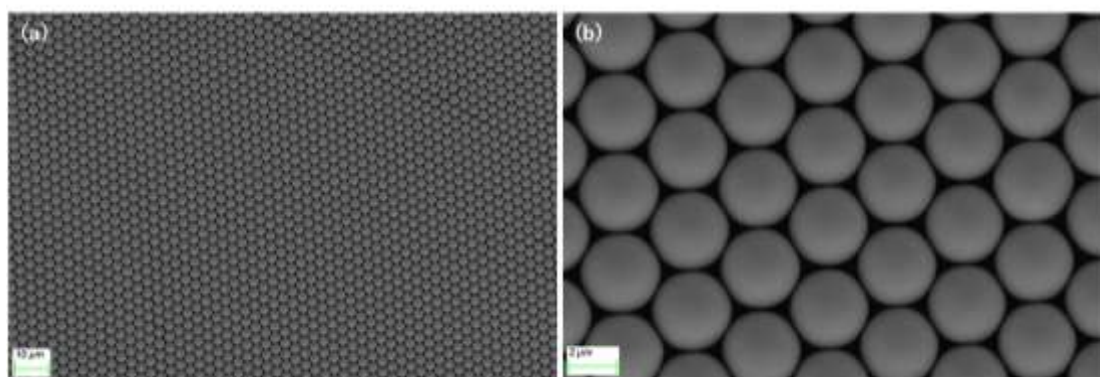


Figure S2. (a, b) SEM images of monolayer PS sphere substrates prepared using the gas-liquid interfacial self-assembly method at different magnifications, with the PS spheres showing a highly ordered arrangement on a large area scale.

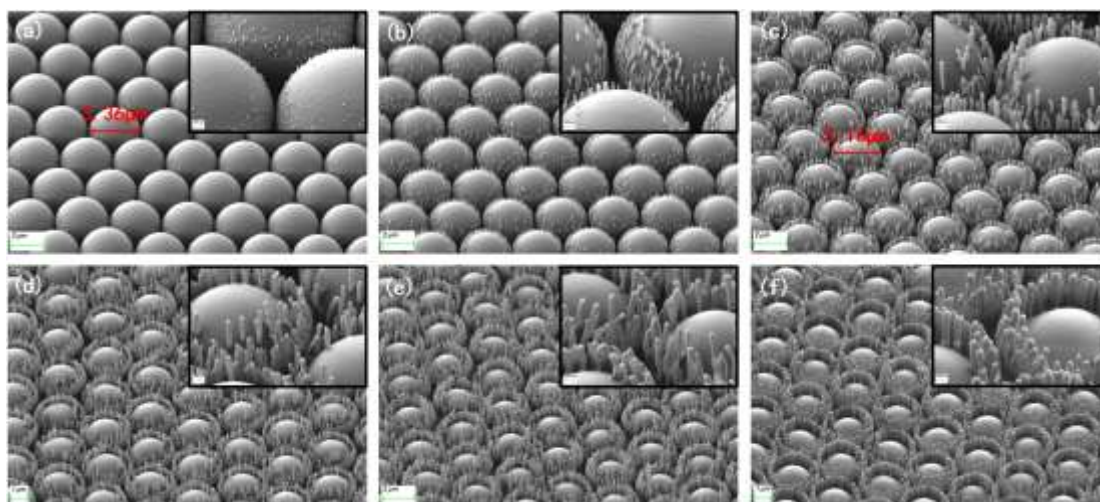


Figure S3. (a-f) SEM images of 100, 200, 300, 400, 500, and 600 s etched in a reactive ion etcher during the preparation of the fence substrate, the insets are magnified images, and the labels in (a, c) are the dimensions of the microspheres measured by the software Image J. As can be seen from the figures, the specific surface area of the substrate increases significantly as the RIE process proceeds. The diameter of the microspheres decreased by 0.2 μm from 3.36 μm to 3.16 μm when going from 100 s to 300 s of etching.

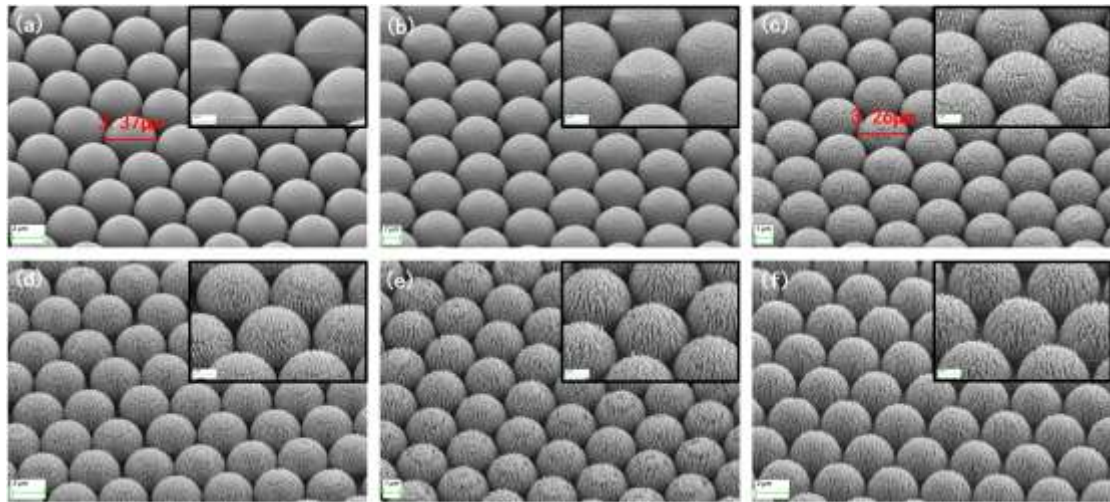


Figure S4. (a-f) SEM images of 100, 200, 300, 400, 500, and 600 s etched in a reactive ion etcher during the preparation of the "hairball" structure, the insets are magnified images, and the labels in (a, c) are the dimensions of the microspheres measured by the software Image J. Similar to the fence structure, the specific surface area of the "hairball" structure increases more significantly during the etching process. The diameter of the microsphere decreases from $3.37\mu\text{m}$ to $3.26\mu\text{m}$ only by $0.11\mu\text{m}$ from 100 s to 300 s, which is lower than that of the fence structure.

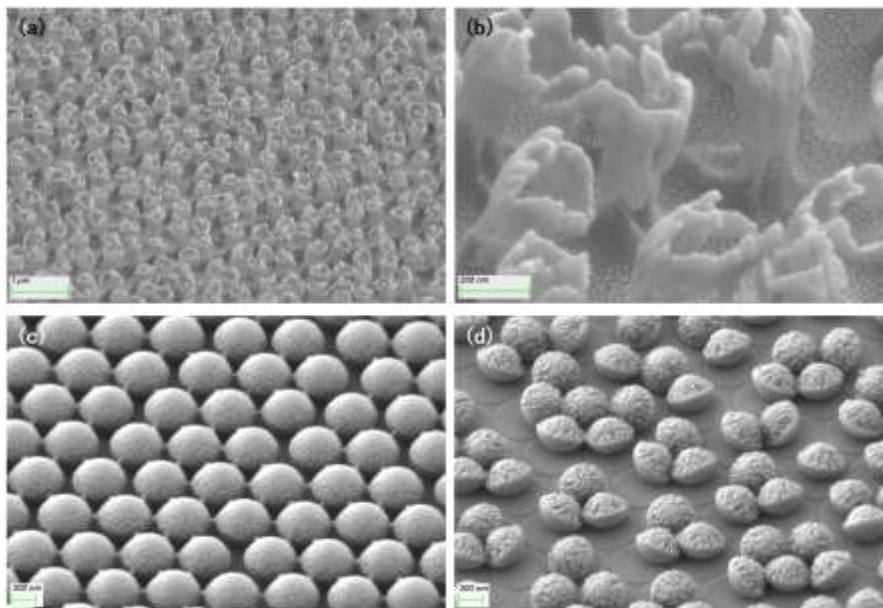


Figure S5. (a, b) SEM images of standing hollow circular cylinder ordered arrays with different multiples; (c) Etching of 500 nm size microspheres using O_2 & CHF_3 for 60 s; (d) etching for 120 s. No expected structure has appeared until etching for 120 s, but the array has collapsed and the microspheres are nearly depleted, making it unnecessary to continue increasing the etching time.

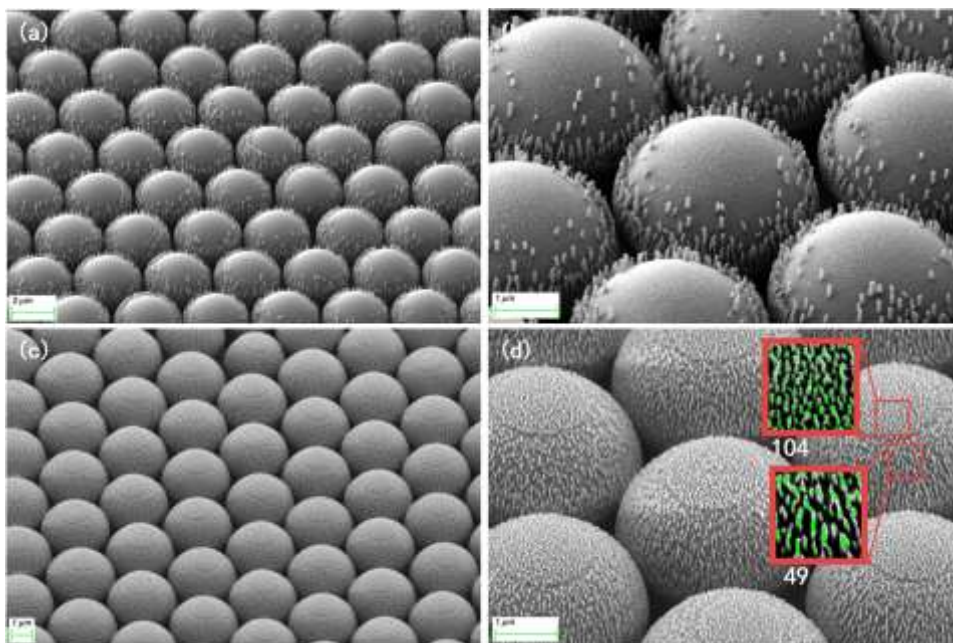


Figure S6. Surface morphology of microspheres under two different atmospheres when RIE was carried out up to 200 seconds. (a, b) and (c, d) are the products obtained by etching the microspheres with a mixture of O_2 with SF_6 and CHF_3 , respectively. The insets are magnified views of areas of $0.25 \mu m^2$ on each side of the demarcation line that we chose to compare regional aggregate density differences. The zoomed-in images have been treated in order to make the aggregates appear more prominent. We labeled the aggregates in it green and counted them, the figures below the inset show the number of aggregates in the region. The results show that the particle density in the top area is $416/\mu m^2$ and that outside the boundary is $196/\mu m^2$.

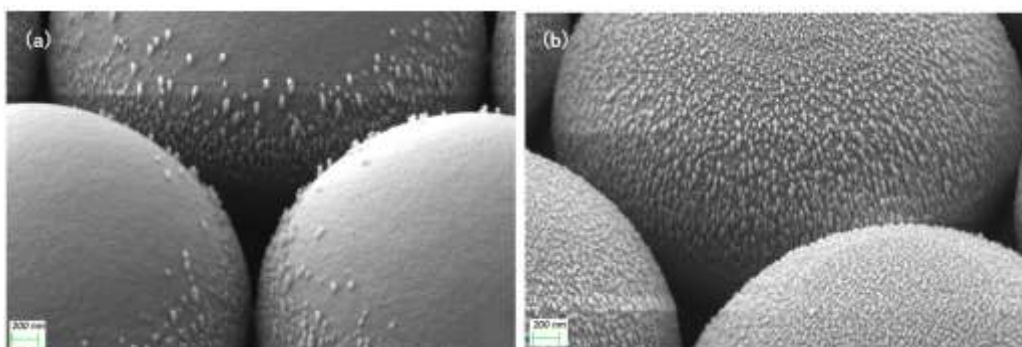


Figure S7. (a, b) Aggregates of AlF_3 particles deposited on the surface of carbonized PS spheres in SF_6 and CHF_3 atmosphere.

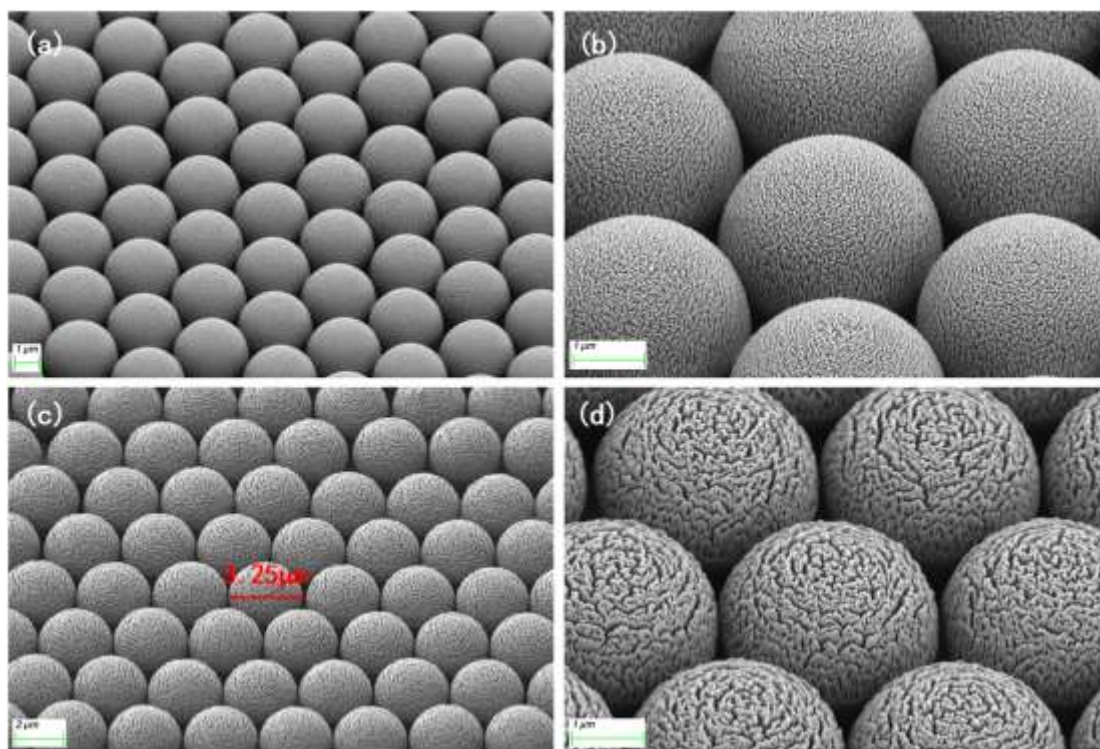


Figure S8. (a, b) SEM images etched in C_4F_8 atmosphere for 200 s; (c, d) SEM images etched in C_4F_8 atmosphere for 600 s. The label in the figure shows the diameter of the microsphere measured by the software Image J after etching for 600 s. The diameter of the microsphere was reduced by $0.25 \mu m$ from etching 0 s to 600 s. This value is close to the diameter reduction of the "hairball" structure from etching 100 s to 300 s, which suggests that the increase in the concentration of C atoms accelerates the carbonization process of the microspheres surface to better protect them from over-etching during the etching process.

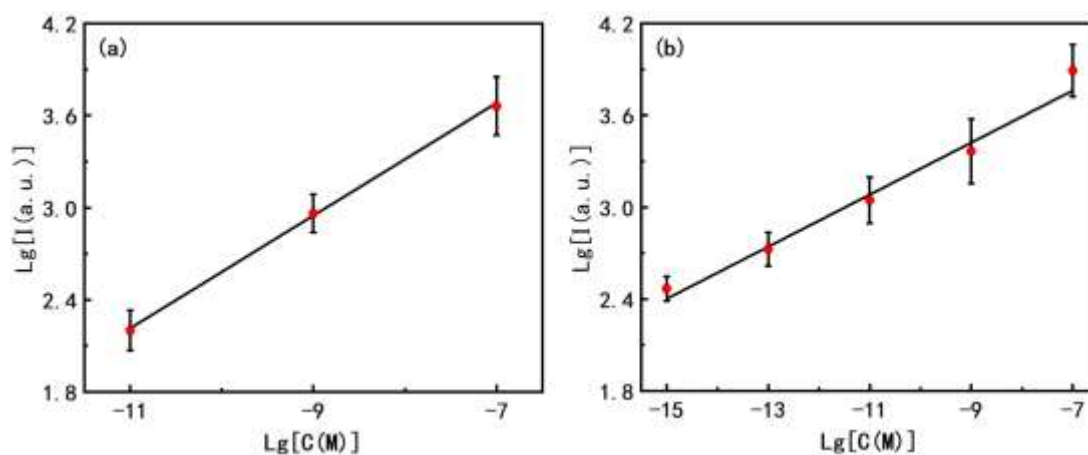


Figure S9. (a) SERS titration isotherm for 4-ATP concentration on fence-structured substrate; (b) SERS titration isotherm for 4-ATP concentration on "hairball" structured substrate.

Table S1. Quantitative elemental analysis by XPS of the fence structure

Component	BE[eV]	FWHM[eV]	RSF	Atomic conc.[%]	Error[%]	Mass conc.[%]	Error[%]
Al 2s	120.00	4.22	0.43	13.1	0.36	16.0	0.42
F 1s	686.00	3.72	1.00	38.9	0.40	33.5	0.36
C 1s	283.00	3.95	0.28	29.7	0.52	16.2	0.35
O 1s	532.00	3.83	0.78	10.2	0.33	7.4	0.24

Table S2. Quantitative elemental analysis by XPS of the "hairball" structure

Component	BE[eV]	FWHM[eV]	RSF	Atomic conc.[%]	Error[%]	Mass conc.[%]	Error[%]
Al 2s	120.80	5.59	0.43	10.9	0.37	18.0	0.55
F 1s	685.80	3.63	1.00	30.7	0.38	35.6	0.42
C 1s	282.80	3.72	0.28	44.2	0.53	32.5	0.48
O 1s	531.80	3.65	0.78	14.2	0.37	13.8	0.36