Monolithic hierarchical gold nanostructures by combined top-down and bottom-up nanofabrication

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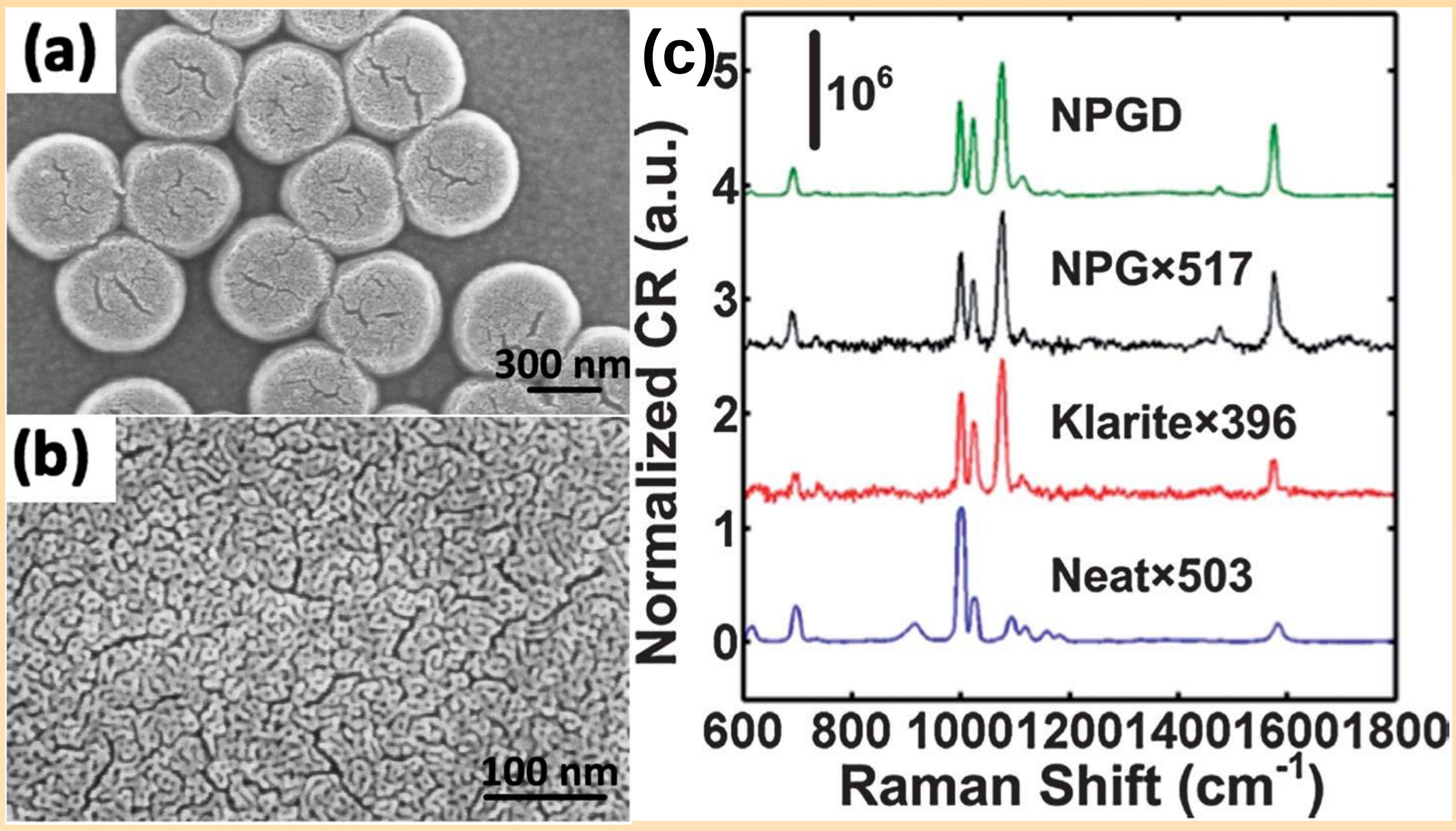
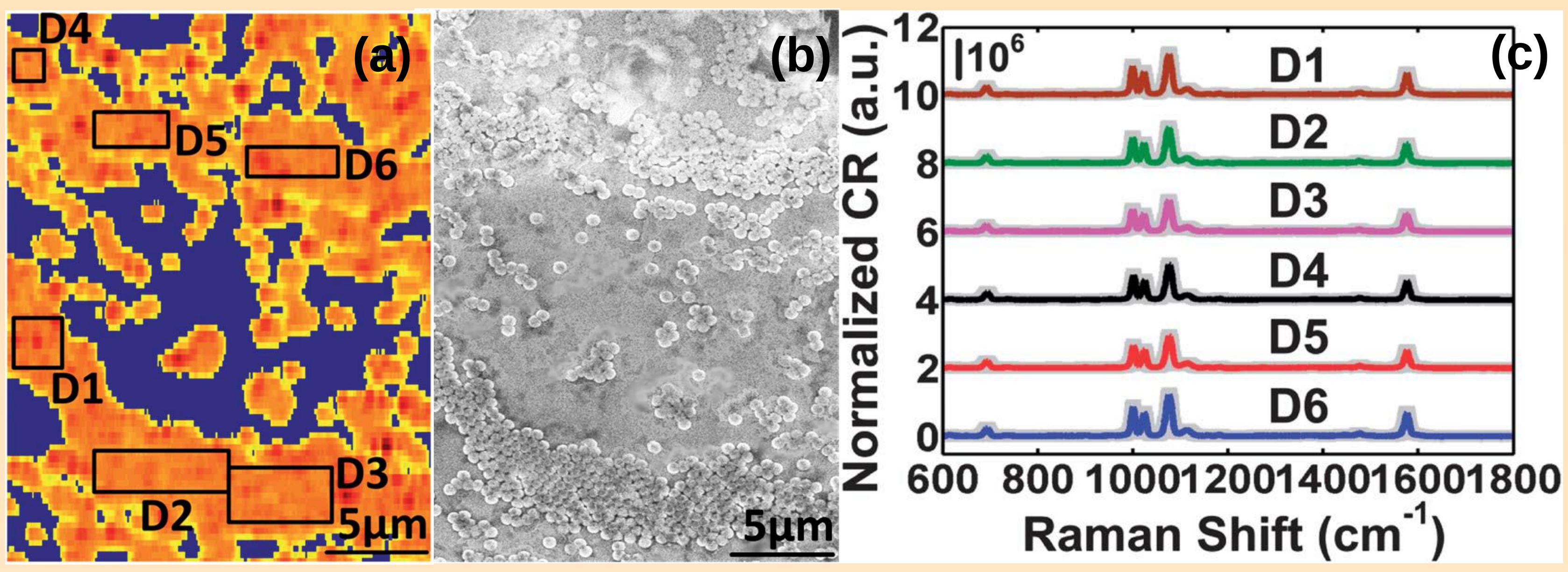
Introduction

- The motivation for this work is that many interesting phenomena occur on surfaces, which exhibit peculiar behavior typically cannot be observed in bulk materials. Unlike dielectric nanomaterials, noble metal nanostructures (e.g., Au) exhibit another peculiarity absent in the bulk, namely, localized surface plasmon resonance (LSPR).
- Nanoporous gold (NPG) produced by selective dealloying features. NPG has been employed as a catalytic substrate for low temperature oxidation. NPG-based microelectrode has enabled advanced electrochemical sensing. The plasmonic properties of NPG have been explored for molecular sensing using "as-dealloyed" films, mechanically stamped films, wrinkled films, and lithographically patterned NPG disks.
- Surface-enhanced Raman scattering (SERS) has been widely applied to molecular detection and identification. A surface-enhanced Raman scattering enhancement factor of at least 10^8 has been reported on monolithic hierarchical nanoporous gold disks.



- (a) Top view of NPGDs ringed by gold; (b) unpatterned NPG film. (c) Normalized count rate (CR) from NPGD, unpatterned NPG, Klarite, and neat benzenethiol vs. Raman shift (cm^{-1}).



(a) SERS map of NPGDs obtained by the line-scan Raman system. (b) SEM image of NPGDs from the same region as in (a). (c) Mean SERS and ±1standard deviation of BT SAMs obtained from 6 areas marked in (a).

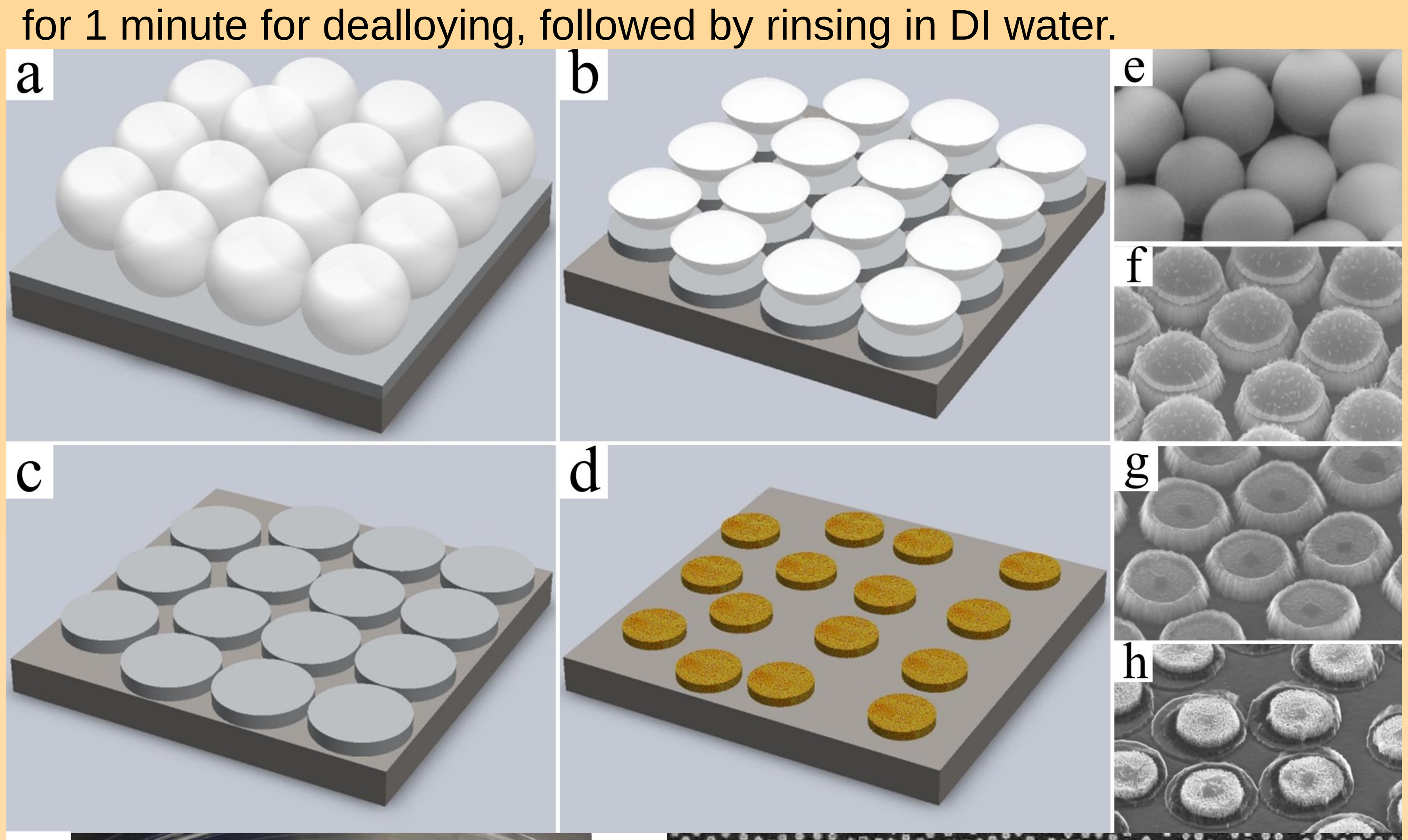
SERS EF estimation using Klarite at 785 nm excitation			
	Klarite	NPGD	NPG film
EF of 1076 cm^{-1}	$1 * 10^6$	$1.05 * 10^8$	$2.03 * 10^5$
EF of 1575 cm^{-1}	$1 * 10^6$	$1.43 * 10^8$	$2.47 * 10^5$

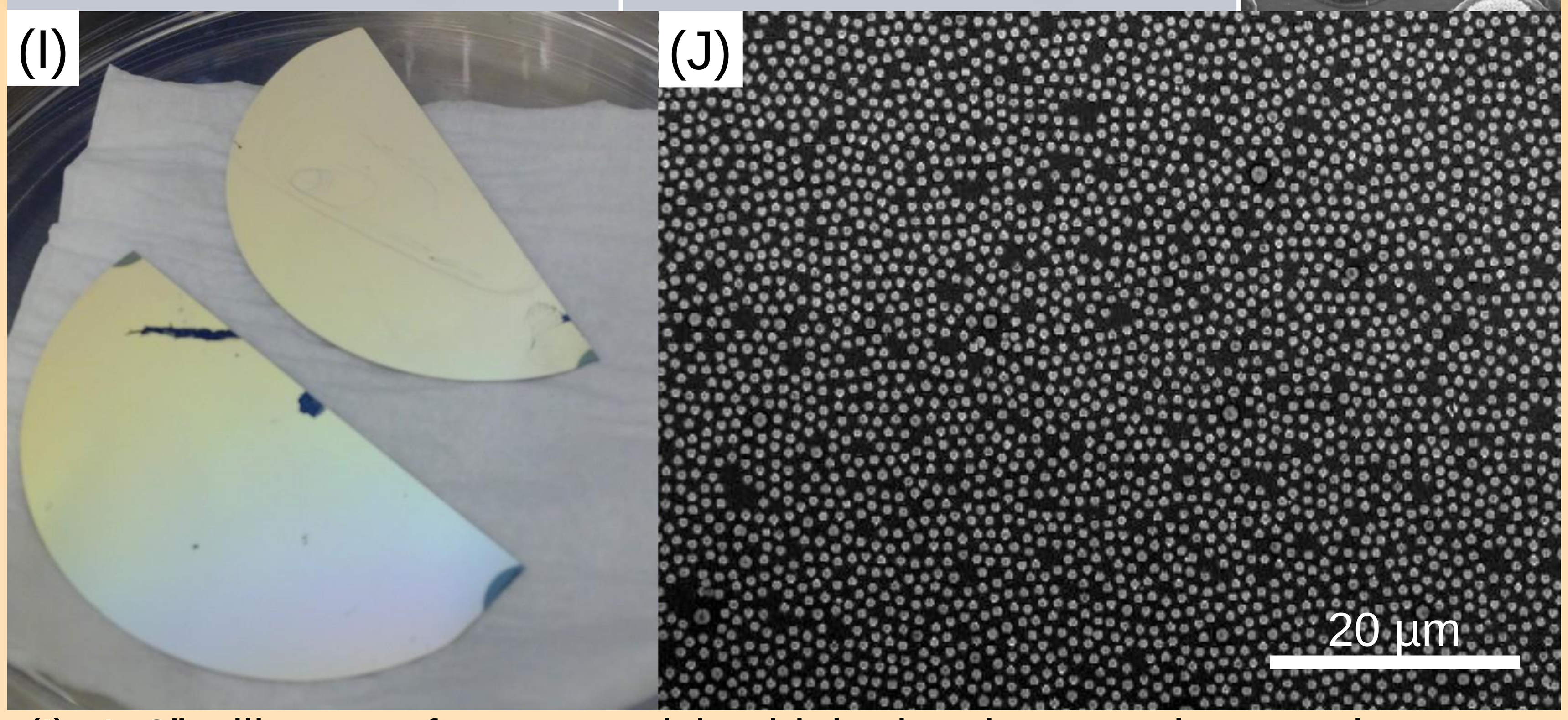
the EF of Klarite is assumed as10^6, although it is specified as at least according to the data sheet, the SERS enhancement factors calculated for 1076 $cm^{-1}$and 1575 cm^{-1} of NPGD substrates are showing above.

- In this work, we present ***shape- and size-controlled*** formation of nanoporous gold disks (NPGD) in high density arrayed formats. Our NPGD features a well-defined "exterior" disk shape, measured 300-700 nm in diameter and 40~75 nm in thickness, and an "interior" 3-dimensional porous network with tunable pore size of 3-30 nm.

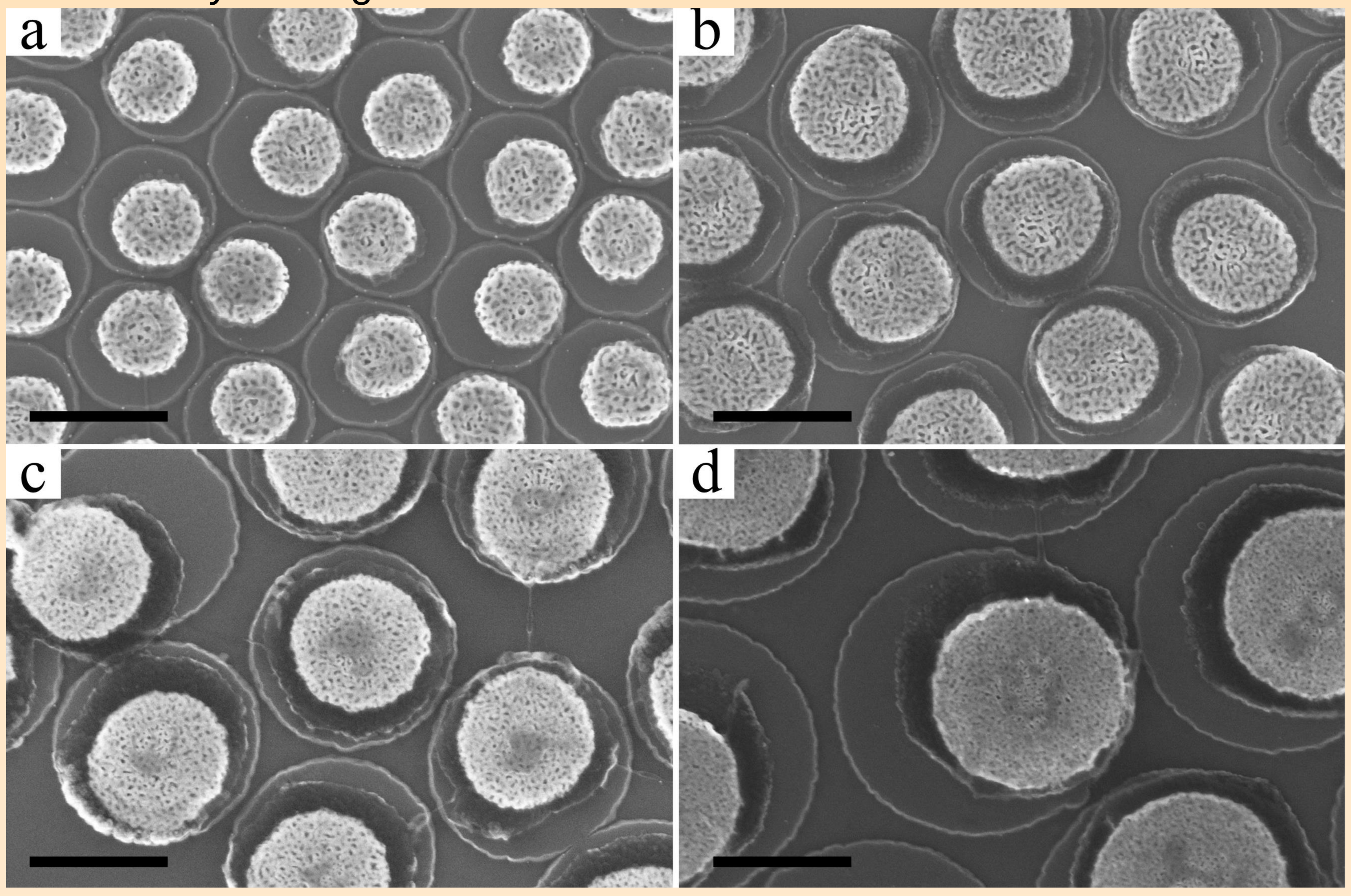
Fabrication Methods & Results

(a, e) ~120 nm thick alloy film was sputtering deposited and a monolayer of polystyrene beads was formed. (b, f) A timed oxygen plasma treatment and sputter etching in argon plasma was employed to transfer the shape into the alloy film. (c, g) Then polystyrene beads were removed (d, h) The alloy disks were then dipped in 70% nitric acid for 1 minute for dealloying, followed by rinsing in DI water.





(I) A 3" silicon wafer covered by high density monolayer polystyrene beads. PS beads coverage >90% was achieved reproducibly. (J) The resulted high density NPGD array. The projected total number of NPGD in one alloy coating run on a 3" wafer is about one billion.



SEM images of nanoporous gold disks made by using 460, 600, 800 and 1100 nm PS beads on Si subsrates. The corresponding diameters are (a) 300, (b) 380, (c) 500 and (d) 700 nm, respectively. The scale bars are 500 nm.

Acknowledgment and References

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Qi, J., et al. (2013). "Surface-enhanced Raman spectroscopy with monolithic nanoporous gold substrates." DOI: [10.1039/C2NR33242F](https://doi.org/10.1039/C2NR33242F) (Communication) *Nanoscale*, 2013, Advance Article.