

Tuneable Surface Enhanced Raman Scattering Metamaterial-like Platforms *via* Three-Dimensional Block Copolymer Based Nanoarchitectures

Carl Banbury¹, Jonathan James Stanley Rickard^{1,2}, Sumeet Mahajan³ and Pola Goldberg Oppenheimer¹

¹School of Chemical Engineering, College of Engineering and Physical Sciences, University of Birmingham, Birmingham, B15 2TT, UK

²Department of Physics, Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge, CB3 0HE, UK

³Department of Chemistry and the Institute for Life sciences, University of Southampton, University Road, Southampton, SO17 1BJ, UK

Surface enhanced Raman spectroscopy (SERS) pushes past the boundaries and inherent weaknesses of Raman spectroscopy, with a great potential for a broad range of applications particularly, for sensing. Yet, current real world applications are limited due to poor reproducibility, low-throughput and stability issues. Here, we present the design and fabrication of self-assembly guided structures based on adjustable block copolymer (BCP) nano-morphologies and demonstrate reproducible SERS enhancement across large areas. Golden three-dimensional (3D) nanostructured morphologies with controllable dimensions and morphologies exhibit high chemical stability, enhanced plasmonic properties and are highly suitable for SERS substrates due to the strong enhancement of the electromagnetic field. Adjustable, free standing porous nanostructures, continuous in the 3D space are achieved by removal of selected BCP constituents. Four BCP morphologies and the corresponding achievable enhancement factors are investigated at 633 and 785nm excitation wavelengths. The choice of excitation laser is shown to greatly affect the observed signal enhancement, highlighting the sensitivity of the technique to the underlying surface architecture and length scales. By using BCP assemblies, it is possible to reliably tune these parameters to match specific applications thus, bridging the gap towards the realization of applied metamaterials. The fabricated SERS platforms *via* three-dimensional block copolymer based nanoarchitectures provide a recipe for intelligent engineering and design of optimised SERS-active substrates for utilisation in the Raman spectroscopy-based devices towards enabling the next-generation technologies fulfilling a multitude of criteria.

INTRODUCTION

Block copolymer (BCP) nano-architectures have been emerging as straightforward and high-throughput platforms for designing and fabricating a range of large-area nanostructures with controllable dimensions, composition and spatial arrangement. Considerable research has been directed toward fabricating and exploiting the self-assembled BCP microphases for their potential implementation into a variety of functional applications including, additives to enable enhanced toughness of plastics and polymer blend composites, guiding the synthesis of nanoparticles [1] acting as capsules for drug delivery, [2] platforms for organic photovoltaics, electronics, data storage and sensors. [3-6] Surface enhanced Raman spectroscopy (SERS) has been concurrently, a topic of extensive scientific investigations in particular, because of its high-sensitivity and specificity for tracing molecular fingerprints, aided by optically excited localised surface plasmon resonances (LSPR), yielding intense local electric fields on metal micro to nanostructures. [7-9] A significant SERS enhancement can be achieved *via* the coupling of the excitations of surface fields to adsorbed or proximal molecules. [10-12] The substrate on which SERS [10, 13-17] is performed is often the crucial factor for successful signal enhancement. However, consistent and controllable fabrication of SERS-active, sensitive and adjustable surfaces still remains challenging. SERS substrates are often limited by instability and lack of tuneability. Since every flaw in substrates has a direct and considerable impact on the ultimate signal, SERS still requires development of methods for designing, fabricating and controlling the surface architecture. Many studies exploit nanoparticle-based systems for SERS enhancement and consequently, their reproducibility, stability and practical applications remain debatable. [18-21] The vast majority of *top-down* synthetic routes to generate nanostructures are based on conventional patterning techniques and are typically expensive, complex and often require precise integration of multistep processes while exhibiting a limited scalability, highlighting the need for more reliable and straightforward lithographic methods to develop efficient

access to *adjustable* three-dimensionally isotropic nanostructures. This has driven extensive efforts to explore novel processes for the fabrication of highly-ordered 3D structures with sub-micrometre periodicities, signposting BCP self-assembly as an alternative *bottom-up* lithographic method, enabling specific orientations from chosen materials on supporting substrates, as a platform for a next generation of miniaturized devices. However, the utilization of self-assembled BCPs for plasmonics, including SERS, has only recently begun to gain traction [9, 22, 23], but still remains predominantly underexplored. Recently, Xin *et al.* reported the use of BCP cylinders integrated with silver nanoparticles for enhancing Raman signals, [24] although for practical SERS applications, gold, being more inert and stable, is more suitable. Furthermore, none of the studies have paid attention to the optimization and tuning possibilities, which can be accessed *via* the range of morphologies of BCP-based substrates for advanced SERS applications. Careful control, understanding and subsequent intelligent engineering can therefore further enable the tailoring of *bottom-up* BCP morphologies for the generation of “hot-spots”; in order to take full advantage of the synergistic functions of the resulting BCP-based SERS architectures.

Here, we demonstrate a range of gold SERS-active 3D nanostructures fabricated from block copolymer self-assembled materials and study their corresponding SERS enhancement and optical properties. Through tailoring the BCP synthesis and tuning the self-assembly, combined with guidance and fabrication of nano-morphologies with characteristic length scales, patterning method and laser frequencies, flexible 3D architectures are fabricated, which are difficult to achieve in another fashion. The fabricated 3D gold SERS substrates are based on block-copolymer microdomain morphologies and comprised of planar (lamellar) structures, cylindrical (both parallel and perpendicular to the supporting substrates) and gyroid (double and free-standing) morphologies. Selective degradation of the self-assembled phase-separated BCP components, plated with a plasmon-active metal (gold) effectively enhances the electromagnetic field, yielding high SERS signals. Consequently, we have designed nanostructured substrates with varying, laser-matching SERS enhancements, which are known to exhibit different Raman signal augmentation at a given excitation wavelength. Characterisation of the photonic properties of 3D BCP-based nano-morphologies revealed that these composite nanostructures behave like new metals with distinct optical characteristics, with a plasma edge shifted to longer wavelengths and a transparency that is greatly increased compared to naturally occurring bulk metal. [25] Substrates with *tunable* (controllable) surface plasmon resonances matching the excitation lasers are essential for gaining the highest enhancements. Broad surface plasmon resonances are needed, especially with red and near-infrared excitation lasers so that high electric fields at both the excitation and Raman scattered wavelengths can be available, to allow for the highest enhancements to be obtained. [26] The obtainable optical properties can be further tuned immensely by variation of the unit cell size, the fill fraction, choice of the BCP morphology and the plasmonic metal used for filling into the template, building upon the various approaches developed to tune the size, shape and spacing of BCP domains and the nanostructures derived from them. [27-31] The architectures fabricated here can provide low-cost, simple, large-active-area substrates, with broad plasmon resonances which open a window for a range of SERS active, easily switchable structures to accommodate various applications towards developing novel, adjustable photonic metamaterials and miniaturised devices.

RESULTS AND DISCUSSION

The phase diagram in **Figure 1** demonstrates the designed and fabricated BCP assemblies containing a range of nanostructured morphologies including, the double gyroid (DG), free-standing gyroid (FSG), mixed combination of parallel and perpendicular to the substrate, (MCYL), hexagonal cylinder domains and only perpendicular cylinders (CYL), accordingly. In the bulk, various morphologies that depend on the relative volume fraction of one block relative to the other produce complex nanostructures due to the micro-phase separation of the BCPs on the molecular scale resulting in a spontaneous formation of a broad spectrum of ordered nanostructures. The evolving nano-morphologies from the BCP melt are

determined by the competition of entropy and the enthalpy between the two blocks and eventually result in the minimisation of the system's energy, yielding the most favourable configurations.

BCP phase morphology typically evolves at the length scale of tens of nanometres and can be controlled by the volume fractions of the constituent blocks, while the total number of monomers N in the BCP chain determines the dimensions of the nanostructure. Lamellar morphology typically results from the alternating symmetric BCP layers while higher levels of one constituting block volume fraction yields asymmetric morphologies comprised of one component forming the minority phase and the other, the matrix phase and finally, with the bi-continuous gyroids (Fig. 1, i) formed between the lamellae (Fig. 1, ii) and the hexagonally packed cylinders, oriented parallel to the substrate. BCP self-assembly of random-coil polymers is a highly efficient process and on supporting surfaces many of the copolymer morphologies exist naturally in a thin film or layer geometries. However, the interactions of the blocks with the surfaces typically results in an orientation of the micro-domains parallel to the substrate, (Fig. 1iii) limiting the successful replication of 'lying' cylinders due to the collapse of the structure following the removal of the matrix during the templating process.

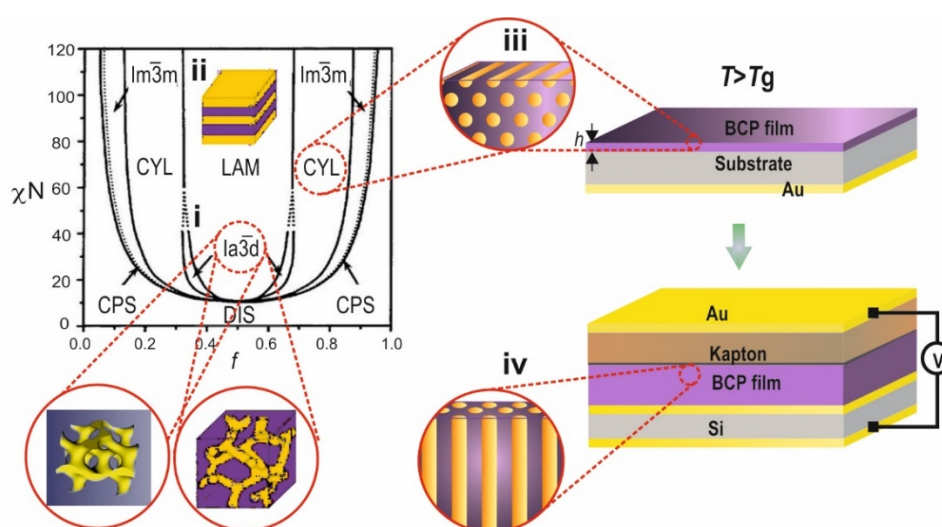


Figure 1. Schematic Representation of the Fabrication of Four Morphologies for SERS Substrates from the Available Self-Assembled Range of BCPs. (i). Three-dimensional gyroid nanostructures comprised of three rotated arms at the three-fold junction with each arm attached to another set. (ii). Tuning the volume fractions of the blocks yields lamellae and cylinder morphologies. (iii-iv) Fabrication of mixed (hexagonal and lying) cylinder arrays and those perpendicular to the substrate (iv) via annealing of PFS-*b*-PLA film above the glass transition temperature, T_g in a capacitor like set-up with an applied E_f of $155 \pm 15 \text{ V}\mu\text{m}^{-1}$, which are solidified by quenching to room temperature. Mixed morphology comprised of a combination of parallel and perpendicular to the substrate cylinders can be generated in-between (iii) and (iv) by controlling the strength of the applied electric field.

Well-defined nanostructures with long-range positional tuning and high-degree of alignment can be achieved by controlling the hydrodynamic flow and the strength of applied field in a microcapacitor device. Therefore, an experimental set-up for exposing BCP films to an electric field, without a gap, was assembled to perpendicularly align the cylinders lying parallel to the supporting substrate inside the BCP thin film. Application of an external electric field, E_f , enables control of the degree of alignment of the hexagonally ordered cylinders, between lying to perpendicular orientations as well as (between Fig. 1iii to iv, accordingly) mixed cylinders morphologies, *i.e.*, MCYL. Annealing above the glass transition temperature of the thin BCP film, without applying an external electric field, results in cylinders which predominantly remain oriented parallel to the substrate with distinctive areas of a terraced-like morphology (Fig. 1 iii) due to the reorganisation of the highly mobile chains in the BCP melt.

Polystyrene-*b*-poly(*d,l*-Lactide) (PS-*b*-PLLA) block-copolymer was used to synthesise the double gyroid nanostructure comprising two interpenetrating, three-dimensional and continuous networks containing 39% fill fraction (Fig. 2a). Selective degradation of the minor phase, while preserving the

majority one in a phase-separated block copolymer morphology, by ultraviolet ozone (UV) etching and *via* a subtle hydrolytic-degradation, yielded a free-standing gyroid template (**Fig. 2b**), which was subsequently coated with inorganic material such as gold (**Fig.3**). Thin films (50-400nm) of poly(ferrocenylsilane)-block-poly lactide (PFS-*b*-PLA), spin-coated onto a *p*-doped silicon wafer (covered with 50nm gold layer on their backside) or on the FTO glass, formed a cylindrical microphase morphology with an ordered block copolymer containing cylinders of PLA in a matrix of PFS, lying in the plane of the film (**Fig.2c**). Cylinder orientation parallel to the film surfaces is typically thermodynamically preferred because of the differing surface energies of the two blocks at one or both interfaces. The electric field guided surface morphology of copolymer cylinders annealed above the glass transition temperature in the capacitor sandwich with an applied voltage of 3-4kV yielding vertically aligned cylindrical nanodomains parallel to the axis of the electric field lines, (**Fig. 2d**) due to the fluctuations of the cylinders around their equilibrium positions and reorganisation of the annealed microphase morphology towards a higher lateral symmetry. In the assembled microcapacitor-device geometry, the electric field results in an aligning torque on the BCP cylindrical morphology and enables control and manipulation of the degree and proportion of the alignment yielding the mixed nanomorphology of MCYL (**Fig. 2d, inset and 3d**). [32, 33]

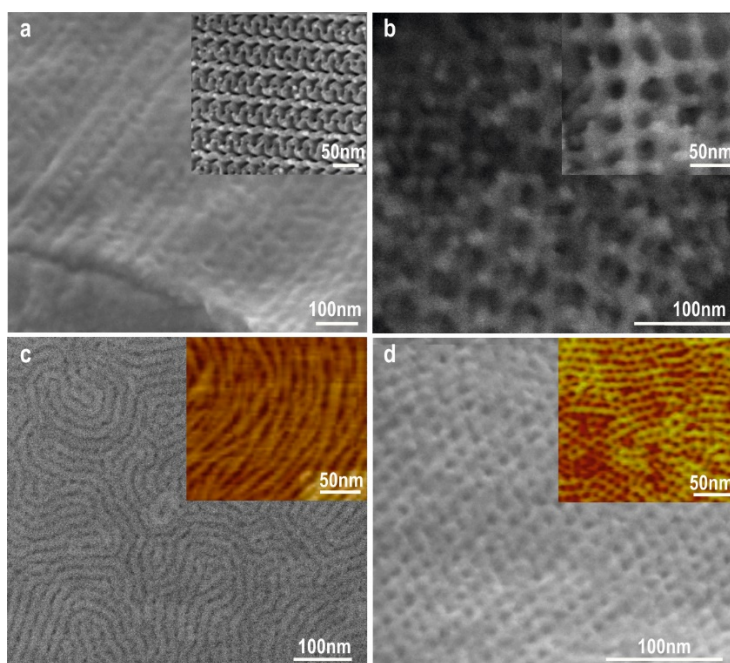


Figure 2. SEM and AFM Characterisation of the BCP-based Nanomorphologies. Tilted (a) and a top-view (a, inset) images of the initially fabricated DG morphology and (b) FSG nanostructures after the selective removal of the minor phase yielding matrix with interconnected networks as a template for further nucleation and growth of inorganic material. (c) As-spun thin BCP film reveals microphase morphology of lying cylinders (inset) which are then reorganised into vertical cylinders (d) mixed with areas of lying cylinders (MCYL) (d, inset) after the electric field application and annealing in a controlled manner.

Subsequently, a range of gold plated nanostructures based on branched 3D organic/inorganic nanohybrids was fabricated. Au coated DG (**Fig. 3b**) and FSG (**Figs. 3a**) interconnected nanonetworks were generated *via* selective degradation of the PLLA phase and plating with gold ($200\pm 30\text{nm}$) *via* electrodeposition or sputtering (see Supporting Information, S1), followed by the UV irradiation, at a wavelength of 254nm, removing the sacrificial organic layer. Hydrolytic removal of the PLA phase in the cylindrical morphologies and the subsequent electroplating of gold nanolayer, provided topographic cylindrical features, visible in the AFM height and cross-sectional low-angle backscattered scanning electron microscopy (LAB-SEM) images, (**Figs. 3c and inset**) revealing vertically organised cylindrical phase morphologies. Absence or existence of a characteristic frequency in the 2-dimensional fast Fourier transform (2D-FFT) power spectrum further helps to identify the lack or existence of the corresponding

periodical structural patterns. The lower symmetry of the 2D-FFT power spectrum, corresponding to the experimentally obtained SEM image, pattern in the inset of **Figure 3d** is indicative of the shorter-range packing in the case of the mixed cylindrical nanomorphologies with a proportion of horizontal and vertical cylinders (**Fig. 3d**).

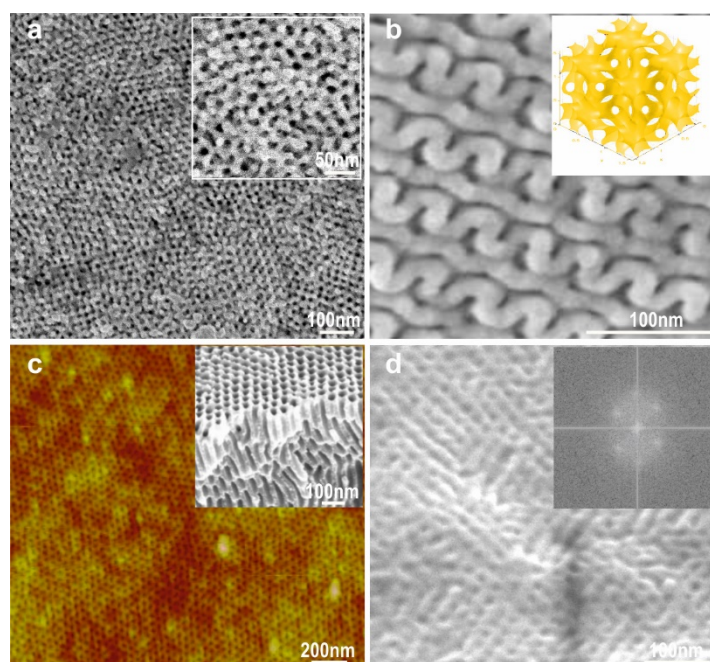


Figure 3. Gold Plated Three-dimensional Nanomorphologies. LAB-SEM images of Au plated and sputtered nanostructures of (a) FSG with a unit cell of 20nm and fill fraction of 39% and (b) DG with the corresponding MATLAB generated simulations of the nanostructure's cell-unit (inset). (c). AFM height image of aligned cylinders continuously spanning the two electrodes with cross-sectional SEM (c, inset) revealing voids left by removal of the minor phase and subsequently gold plated and sputtered. (d). Surface SEM of the Au coated mixed cylindrical morphology after UV ozone etching of PFS matrix with the FFT of the image (inset).

SERS performance of the four fabricated nanostructures was evaluated through adsorbing a monolayer of benzenethiol, as a Raman probe, from a 10 μ M ethanolic solution on each gold nanosurface (**Fig. 4a**) at excitation wavelengths of 633 and 785nm as well as using rhodamine 6G (R6G) as Raman active molecule (see Supporting Information, S3). [17, 34, 35] Notably, SERS spectra of BT exhibit difference in intensity of the Raman bands at different excitation wavelengths. While strong Raman bands at 1000, 1027 and 1070cm⁻¹, corresponding to the aromatic ring breathing modes, *in-plane* C-H deformation and rocking vibrations of benzene are observed under excitation of both 633 and 785nm, at the shorter laser wavelength of 633nm additional Raman bands, above 1300cm⁻¹ are also enhanced. The absolute enhancement factor (EF) (**Fig. 4b**) for the FSG based SERS substrate was found to be 6.1 \times 10⁷ and 6.7 \times 10⁷ at 785 and 633nm, respectively. For the other three nanostructures of CYL, MCYL and DG, the EF was consistently higher at 785nm excitation laser with 38% increase in enhancement for the CYL (EF=4.5 \times 10⁷ and 3.2 \times 10⁷ at 785 and 633nm, respectively) and 61% for the MCYL (EF=5.0 \times 10⁷ and 1.9 \times 10⁷ at 785 and 633nm, respectively) in comparison to excitation with a 633nm laser. The smallest enhancement was observed for the DG based SERS nanostructures with EF of 2.6 \times 10⁶ at 785nm and 9.6 \times 10⁵ at 633nm. The substrates exhibited a good SERS signal reproducibility which was established by examining random areas ($n=10$) across each surface under identical experimental conditions using benzenethiol monolayer as the SERS probe, yielding similar relative peak intensities. Uniform and consistent SERS signals were detected from different locations across each sample area with the correlated SERS based enhancement factor calculation, (see Supporting Information, S2) demonstrating that the values are narrowly distributed around the average of 8.2 \times 10⁷ \pm 1.2 \times 10⁷, 4.5 \times 10⁷ \pm 2.3 \times 10⁷,

$6.6 \times 10^7 \pm 8.9 \times 10^6$ and $3.5 \times 10^6 \pm 1.3 \times 10^6$ for FSG, CYL, MCYL and DG, accordingly (Fig. 4c). Based on the 0.95 confidence interval data, we therefore expect the difference in enhancement factor as measured between the different areas to lie between $(5.8 \times 10^7, 1.1 \times 10^8)$, $(4.6 \times 10^7, 9.0 \times 10^7)$, $(4.9 \times 10^7, 8.4 \times 10^7)$ and $(7.8 \times 10^5, 6.1 \times 10^6)$ for FSG, CYL, MCYL and DG, respectively, 95% of the times in future measurements. Importantly, all the EFs are on the same order of magnitude of $\times 10^7$ (for FSG, MCYL and CYL) and $\times 10^6$ (for DG) with the small variation in the pre-factor values, with the largest difference in the SERS EFs of less than 7 fold for the DG and less than 2 fold for both the for the MCYL and the FSG (Fig. S2), indicating good signal reproducibility in agreement with the typical SERS platforms, considered highly similar even when showing a nearly 1 order of magnitude difference. [36] The EF achieved with these morphologies is of similar or higher magnitude to the commercially available SERS substrates such as for instance, Mesophotincs, [37] ST Japan, [38] Stellnet Inc. [39].

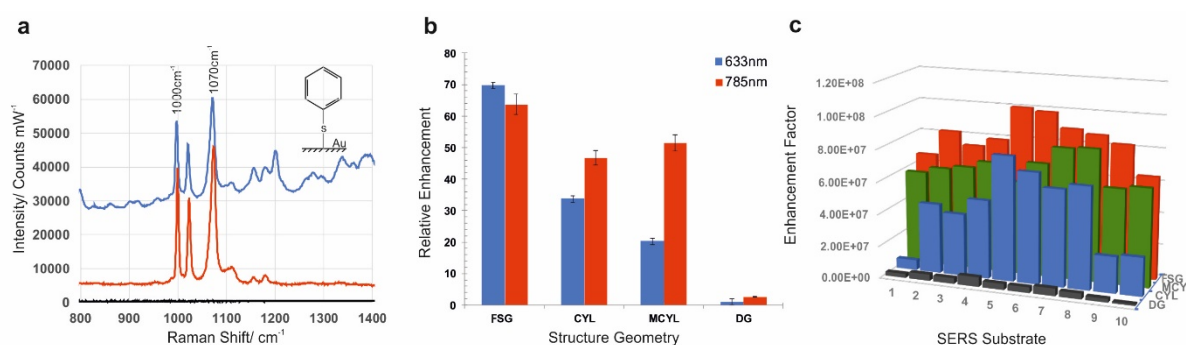


Figure 4. BCP-based SERS Substrates. (a). Representative SERS spectra of benzenethiol (inset) recorded from substrates excited with a 633nm (blue) and 785nm (red) lasers with typical Raman bands at 1000 and 1070 cm^{-1} of the aromatic ring deformation vibrations. (b). Relative SERS enhancement of the 1070 cm^{-1} peak with the highest signal enhancement obtained for the FSG with 633nm followed by MCYL with 785nm. (c). The average SERS enhancement factors (EFs) of the 3D SERS-active nanomorphologies across ten areas on each substrate indicate uniform properties across the structured area with EFs of the order of 10^{7-8} for FSG and MCYL and only 10^{5-6} for the DG nanostructures.

Interestingly, only for the FSG nanostructure, the relative SERS enhancement of benzenethiol molecules was found to be both the highest as well as greater while using the 633nm laser *versus* the 785nm, in comparison to the rest of the nanoarchitectures, for which the 785nm yielded higher enhancement of the signal relative to the 633nm. Furthermore, the MCYL SERS surface demonstrated the biggest increase in enhancement using the 785nm excitation laser *versus* the 633nm, greatly exceeding the DG nanostructure, which showed the lowest EF amongst the fabricated substrates (1.9×10^7 compared to 9.6×10^5) (Fig. 4b). This can be explained by the fact that SERS enhancement effect is dependent on the wavelength and mainly arises from the LSPRs of the nanoarchitectures and therefore, a particular SERS substrate will exhibit highest enhancement at a certain excitation wavelength. These results indicate that the FSG is the optimal nanostructure to be exploited with the 633nm excitation laser to yield the highest enhancement. However, since BCP morphologies that are bicontinuous in all three spatial dimensions are still rare and difficult to manufacture in particular, over large areas, the MCYL morphology presents itself as a particularly promising and viable candidate as a strong SERS enhancing substrate with a 785nm laser. Since the shape of the nano-morphology plays an important role in SERS, and the electromagnetic enhancement is strongly dependent on the surface morphology and precise shape of the features at the metal surface, the optimal SERS enhancement requires a delicate balance between the excited and scattered wavelengths with the plasmon peak of the metal nanostructure. A plasmon which can be excited at the scattered wavelength out-couples the Raman scattered radiation more efficiently. This is important especially in the near infra-red, where the laser excitation and the Raman scattered radiation can be significantly different in terms of wavelength and hence, excitation or existence of plasmonic absorption at one of these is not sufficient for obtaining the highest SERS enhancements.

While the SERS activity of the plasmonic BCP-morphologies is promising for detection applications due to uniform and high EFs the optical properties of these metamaterials themselves are interesting. New optical properties emerge, different to bulk gold in these metamaterial-like nanostructures. **Figure 5** shows the transmittance spectra recorded with unpolarised light in the visible range on each gold-plated nanostructure sample (**Fig. 5, inset**). The spectra are normalised relative to the transmission from a smooth gold film on the same supporting substrate.

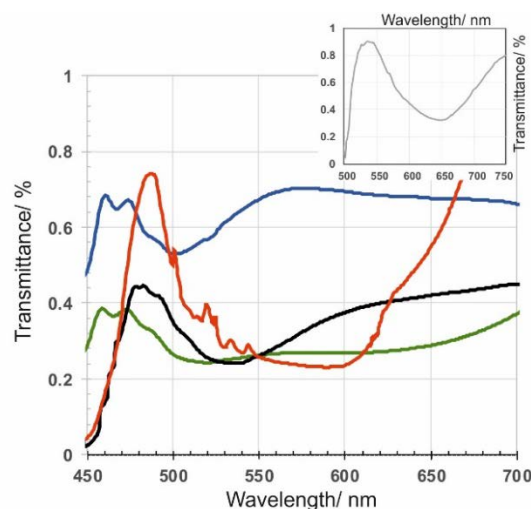


Figure 5. Optical Properties of Gold-plated Nanostructures. Spectroscopic characterisation of the optical behaviour for transmission configuration with unpolarised incident light for each BCP-based nanomorphology (red: FSG, green: MCYL, blue: CYL and black: DG) with characteristic extinction peaks compared to a gold layer of similar thickness. The blue shift is consistent with what predicted and measured for metamaterials and porous gold and is due to a reduction in the average electron density of the nanostructure and an increase in the self-inductance of the interconnected network of gold.

For the gold infiltrated nanomorphologies there is a distinct change in the position of the extinction wavelength maximum. For the FSG, a characteristic extinction peak in the transmission is observed around 600nm, which shifts progressively to higher energy of 485nm for CYL, 520nm for MCYL and 540nm for the DG. The MCYL extinction maximum at 520 nm is qualitatively similar to that of bulk 'solid' gold however, while in the latter case the absorption is related to inter-band transitions, here it is attributable to multi-domain structure as the plasma frequency is inherently modified by the nanostructuring and corresponding air-filling fraction. [40] For single gyroid metamaterials fabricated in gold, properties such as enhanced transmission have been previously observed due to their sub-wavelength architectures and the arising plasmon resonances. [25] The transmission spectrum in **Figure 5** of FSG nanostructure is qualitatively similar to that shown for single gyroids previously. The difference in the maximum extinction wavelength at 600nm compared to the one reported by Salvatore *et al.* [25] is attributed to the twenty nanometre unit cell size in the fabricated structures. For DG structures, very low transmission is observed. This is not unsurprising as Hur *et al.* have previously predicted a different mechanism of propagation of surface plasmons in double gyroid metamaterials. [41] The existence of two interpenetrating continuous plasmon metal networks induces local capacitance and alters the surface plasmon propagation. Thus, losses can be higher and also significantly dependent on each of the interpenetrating structures *e.g.*, their relative fill-fraction or size of struts. To note, that while the SERS enhancements of the substrates and the optical properties are related, the optical properties of metamaterials, even though fabricated from plasmonic materials, are dominated by those due to their intrinsic structure. Plasmon length scales are of the order of ~100nm, while metamaterials such those demonstrated here have <10nm length scales. The SERS enhancements which are observed in our case provide clear evidence that plasmons are excited in these metamaterials. However, the optical transmission spectra indicate that the optical properties are more than due to plasmonic absorption only

with the understanding of the extraordinary optical properties of novel plasmonic metamaterials being an area of an active, ongoing research. [42]

CONCLUSIONS

The guided self-assembly of the BCP blocks offers a unique platform for structuring materials with tuneable sizes on the nanoscale thus, offering a great variability of structural features by the independent control of experimental parameters in a robust manner, generating high-fidelity consistent nanoarchitectures across large substrate areas and subsequently, enabling reliable manufacture of substrates with high SERS enhancements. The optical properties of these nanomaterials are found to be distinguished primarily by the morphology, length scale and periodicity on which the constituent materials are structured. The tuning of plasmon resonances can further be accomplished by controlling the dimensions (size and periods) of the microphase-separated nanostructures, through alteration of the molecular weight and composition which in turn, will allow the design of SERS substrates that generate strong localized electromagnetic fields at optical wavelengths that are required for the optimum SERS excitation by different laser sources thus, harnessing such inherently precise self-assembly behaviour of BCPs towards the realization of 3D metamaterials. Dimensional control of the nano-morphologies combined with theoretical modelling could further improve the BCP-based SERS substrates and the enhancements that can be obtained from them and is currently underway. Finally, establishing of such a technique might also provide the missing-link towards the realization of applied metamaterials, heralding a new era for developing novel types of optical materials from BCP self-assembly origin and their integration into composite functional devices.

ACKNOWLEDGEMENTS

We acknowledge funding from the Wellcome Trust (1741SSFP) and the Royal Academy of Engineering (RF1415\1428). P.G.O. is a Royal Academy of Engineering Research (RAEng) Fellowship holder. C. Banbury gratefully acknowledges funding from EPSRC through a studentship from the Sci-Phy-4-Health Centre for Doctoral Training (EP/L016346/1).

EXPERIMENTAL

Sample Preparation. The samples were prepared using the PFS-*b*-PLA and PS-*b*-PLLA block-copolymers (volume fraction, $f = 39\%$) with thin films spin-coated from a 5-10wt/wt%, from toluene, onto Au-coated *p*-doped silicon wafers or transparent FTO glass substrates. The minority component was subsequently removed either by UV etching (15 minutes at 254nm) or exposure to plasma system (10 minutes, O₂ plasma) under controlled low pressure conditions. In order to release the BCP film prior or post degradation and for imaging purposes, the underlying gold layer was removed *via* etching in 80:1 bromine to methanol solution. The resulting nanostructures were plated *via* electrodeposition with Au with an initial nucleation step between 0.0 and -1.2V at a scan rate of 50mV/s (average of 3 CV scans) followed by the deposition step (100s, -0.8V) up to a thickness in ranges between 200-300nm. [43] A reaction kinetics-controlled region (from -0.2 to -0.75V) was followed by a mass transport-controlled region (from -0.8 to -1V), featuring a cathodic peak characteristic of diffusion-controlled electroplating processes. As the electroplating process was used to obtain nanometre Au layers, the gold growth rate was slow enough to enable careful control over the deposition process, generally achieved in the kinetics-controlled region, where the applied over-potential with respect to the OCP value is small and therefore, acts as the gold deposition driving force. Plating at $E = -0.8V$, the electrochemically-driven Au³⁺ reduction occurred at the working electrode with a high deposition rate, leading to the formation of a large number of initial nuclei which ultimately grow to overlap and form a full layer with an average representative thickness of 200nm (at 100s deposition time). [44] The nanostructures were alternatively (or additionally) covered with a thin Au film using an Emitech sputter-coater with a DC Ar plasma (gold target purity 99.999%, Kurt J. Lesker Company) with two cycles of 10s at 55mA were carried out.

Alignment of BCP Using an Electric Field. BCP thin film was spin-coated onto a supporting conductive substrate, serving as a bottom electrode, of either silicon with a nanometre gold layer evaporated on the back side of it or FTO glass with a thin layer of silver paste around the edge of the substrate. A capacitor-like device was subsequently assembled with vertical electric field applied generated across it (a constant high-voltage of 4kV was applied across the assembled capacitor device), while the BCP film was annealed above the glass transition temperature of both constituent blocks ($T_{g(\text{PFS})} = 103^{\circ}\text{C}$ and $T_{g(\text{PLA})} = 57^{\circ}\text{C}$). The opposing electrode was a 20 μm thick sheet of Kapton with a 50nm evaporated gold layer on the bottom side along with a thin layer of 2 μm of poly(dimethylsiloxane) (Sylgard 184, Dow-Corning) spin-coated on front of it to establish a conformal contact with the BCP film.

Atomic Force Microscopy. NanoScope IV Multimode and Dimension 3100 (Digital Instruments, Santa Barbara, CA) atomic force microscope was used to thoroughly characterise the surfaces' topography. The AFM measurements were performed using tapping mode *via* an intermittent contact of the tip with the sample, in ambient conditions. NSG 20 cantilevers with a resonance frequency of 260 kHz and a stiffness of 28Nm⁻¹ were used. Height and phase images were analysed with the Nanoscope software (Digital Instruments). To improve contrast, patterns were exposed to UV-light and rinsed in cyclohexane to remove some of the PS phase.

Scanning Electron Microscopy. Samples for SEM imaging were prepared by placing a post-experiment, disassembled substrate with the generated patterns on an inclined or cross-sectional holder to enable the imaging of the top and cross-sectional views. Scanning electron micrographs were acquired using a thermally assisted Field Emission Scanning Electron Microscope (FESEM, LEO VP 1530 and FEI Magellan and Helios) with a lateral resolution of 1-5 nm. A LEO ULTRA 55 SEM instrument including a Schottky emitter (ZrO/W cathode) was also used for imaging the samples with a typical acceleration voltage of 2-5kV equipped with the energy dispersive X-ray spectroscopy (EDX). Scanning transmission electron microscope (STEM) images were obtained using Hitachi s5500 with a cold field-emission source and lens detector with 4Å resolution, allowing adjustable acceptance angle STEM imaging. Low-angle backscattered electrons imaging mode was used to contrast the as-spun and those gold replicated samples, providing the atomic number contrast. The power spectrum results of BCP nanostructure images were obtained with the image analysis program (ImageJ) applying a 2D-FFT algorithm.

SERS Measurements. SERS measurements were carried out using micro Raman spectroscopy system with *InVia* Qontor *spectrometer* for confocal Raman (Renishaw *Plc.*) equipped with 514, 633 and 785 nm lasers which was adjusted for optimal throughput, fluorescence control and sensitivity. Benzenethiol was adsorbed onto the gold surface by soaking in a 10 μM solution in ethanol for 30min. The samples were then rinsed with ethanol and left to dry in air for 15min before measurement. The spectra were typically acquired at 10s exposure time and a laser power of 1 to 3mW to avoid photochemical effects in the SERS spectra, sample damage or degradation. SERS maps were generated in a Streamline mode scan with 10s exposure time and 50mW power at 633 and 785nm. A 50x objective with a numerical aperture of 0.75 was used for SERS measurements over a range of 500 to 1600cm⁻¹ relative to the excitation Raman shift. Optical measurements were carried out with a specially adapted research grade microscope (Leica DM 2700M) equipped with incoherent white light source, allowing confocal measurements with 2.5 μm depth resolution. The spectra were normalized with respect to those recorded on flat gold or gold covered flat copolymer film surfaces. An intelligent fitting filter was applied for baseline subtraction. After excluding regions with peaks, the baseline was fitted to all the remaining points in each spectrum and a polynomial order of eight with the noise tolerance of 1.50 was applied.

Optical Characterisation. Leica DM200 optical polarizing microscope was used to investigate the optical texture of the samples. The optical transmission characterisation of the samples was evaluated in terms of variations of the intensity of transmitted light using unpolarised incident light and the attached spectrometer (Horiba). The microscope Xenon lamp acted as an illumination source for the spectroscopic measurements. 100 mm optical fibre (ThorLabs) in the focal plane of x20 microscope objective working distance has served as pinhole for the signal collection. Motorized MicroHR Imaging Spectrometer with solid state UV coated Silicon over Indium Gallium Arsenide detector for 200nm-1700nm and the SynerJY for Windows software were used for data acquisition and analysis.

REFERENCES

1. Ray, D., V.K. Aswal, and J. Kohlbrecher, *Synthesis and Characterization of High Concentration Block Copolymer-Mediated Gold Nanoparticles*. Langmuir, 2011. **27**(7): p. 4048-4056.
2. Adams, M.L., A. Lavasanifar, and G.S. Kwon, *Amphiphilic block copolymers for drug delivery*. Journal of Pharmaceutical Sciences, 2003. **92**(7): p. 1343-1355.
3. Darling, S.B., *Block copolymers for photovoltaics*. Energy & Environmental Science, 2009. **2**(12): p. 1266-1273.
4. Goldberg-Oppeneheimer, P., et al., *Hierarchical Orientation of Crystallinity by Block-Copolymer Patterning and Alignment in an Electric Field*. Chemistry of Materials, 2013. **25**(7): p. 1063-1070.
5. Park, T.H., et al., *Block copolymer structural color strain sensor*. NPG Asia Materials, 2018.
6. Segalman, R.A., et al., *Block Copolymers for Organic Optoelectronics*. Macromolecules, 2009. **42**(23): p. 9205-9216.
7. Bezares, F.J., et al., *The Role of Propagating and Localized Surface Plasmons for SERS Enhancement in Periodic Nanostructures*. Plasmonics, 2012. **7**(1): p. 143-150.
8. Caldwell, J.D., et al., *Plasmonic Nanopillar Arrays for Large-Area, High-Enhancement Surface-Enhanced Raman Scattering Sensors*. ACS Nano, 2011. **5**(5): p. 4046-4055.
9. Hu, W. and S. Zou, *Proposed Substrates for Reproducible Surface-Enhanced Raman Scattering Detection*. The Journal of Physical Chemistry C, 2011. **115**(11): p. 4523-4532.
10. Barnes, W.L., A. Dereux, and T.W. Ebbesen, *Surface plasmon subwavelength optics*. Nature, 2003. **424**: p. 824.
11. Kneipp, K., et al., *Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS)*. Physical Review Letters, 1997. **78**(9): p. 1667-1670.
12. Nie, S. and S.R. Emory, *Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering*. Science, 1997. **275**(5303): p. 1102-1106.
13. Kho, K., et al., *Polymer-based microfluidics with surface-enhanced Raman-spectroscopy-active periodic metal nanostructures for biofluid analysis*. Vol. 13. 2008. 054026.
14. Mahajan, S., et al., *Relating SERS Intensity to Specific Plasmon Modes on Sphere Segment Void Surfaces*. The Journal of Physical Chemistry C, 2009. **113**(21): p. 9284-9289.
15. Ozbay, E., *Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions*. Science, 2006. **311**(5758): p. 189-193.
16. Pennathur, S. and D. Fygenson, *Improving fluorescence detection in lab on chip devices*. Vol. 8. 2008. 649-52.
17. Pola, G.O., M. Sumeet, and S. Ullrich, *Hierarchical Electrohydrodynamic Structures for Surface-Enhanced Raman Scattering*. Advanced Materials, 2012. **24**(23): p. OP175-OP180.
18. Lim, C., et al., *Optofluidic platforms based on surface-enhanced Raman scattering*. Analyst, 2010. **135**(5): p. 837-844.
19. Piorek, B.D., et al., *Free-surface microfluidic control of surface-enhanced Raman spectroscopy for the optimized detection of airborne molecules*. Proceedings of the National Academy of Sciences, 2007. **104**(48): p. 18898-18901.
20. Qian, X., X. Zhou, and S. Nie, *Surface-Enhanced Raman Nanoparticle Beacons Based on Bioconjugated Gold Nanocrystals and Long Range Plasmonic Coupling*. Journal of the American Chemical Society, 2008. **130**(45): p. 14934-14935.
21. Lutz, A., A. Andreas, and B. Robert, *Catalytic Arylation Reactions by C/H Bond Activation with Aryl Tosylates*. Angewandte Chemie International Edition, 2006. **45**(16): p. 2619-2622.
22. Han-Yu, H., et al., *Well-Defined Multibranching Gold with Surface Plasmon Resonance in Near-Infrared Region from Seeding Growth Approach Using Gyroid Block Copolymer Template*. Advanced Materials, 2013. **25**(12): p. 1780-1786.
23. Wang, Y., et al., *Nanostructured Gold Films for SERS by Block Copolymer-Templated Galvanic Displacement Reactions*. Nano Letters, 2009. **9**(6): p. 2384-2389.

24. Zhang, X., et al., *Silver based SERS substrates fabricated from block copolymer thin film*. 2013. 34006.
25. Stefano, S., et al., *Tunable 3D Extended Self-Assembled Gold Metamaterials with Enhanced Light Transmission*. *Advanced Materials*, 2013. **25**(19): p. 2713-2716.
26. Mahajan, S., et al., *Reproducible SERRS from structured gold surfaces*. *Physical Chemistry Chemical Physics*, 2007. **9**(45): p. 6016-6020.
27. Vriezেকolk, E.J., et al., *Control of pore size and pore uniformity in films based on self-assembling block copolymers*. *Journal of Polymer Science Part B: Polymer Physics*, 2014. **52**(23): p. 1568-1579.
28. Radjabian, M. and V. Abetz, *Tailored Pore Sizes in Integral Asymmetric Membranes Formed by Blends of Block Copolymers*. *Advanced Materials*, 2015. **27**(2): p. 352-355.
29. Gu, Y. and U. Wiesner, *Tailoring Pore Size of Graded Mesoporous Block Copolymer Membranes: Moving from Ultrafiltration toward Nanofiltration*. *Macromolecules*, 2015. **48**(17): p. 6153-6159.
30. Guo, T., et al., *Hierarchically Porous Organic Materials Derived From Copolymers: Preparation and Electrochemical Applications*. *Polymer Reviews*, 2018: p. 1-38.
31. Dorin, R.M., et al., *Designing block copolymer architectures for targeted membrane performance*. *Polymer*, 2014. **55**(1): p. 347-353.
32. Crossland, E.J.W., et al., *A Bicontinuous Double Gyroid Hybrid Solar Cell*. *Nano Letters*, 2009. **9**(8): p. 2807-2812.
33. Pola, G.O., E. Dominik, and S. Ullrich, *Carbon Nanotube Alignment via Electrohydrodynamic Patterning of Nanocomposites*. *Advanced Functional Materials*, 2011. **21**(10): p. 1895-1901.
34. Biggs, K.B., et al., *Surface-Enhanced Raman Spectroscopy of Benzenethiol Adsorbed from the Gas Phase onto Silver Film over Nanosphere Surfaces: Determination of the Sticking Probability and Detection Limit Time*. *The Journal of Physical Chemistry A*, 2009. **113**(16): p. 4581-4586.
35. Tian, F., et al., *Surface enhanced Raman scattering with gold nanoparticles: effect of particle shape*. *Analytical Methods*, 2014. **6**(22): p. 9116-9123.
36. Ansar, S.M., et al., *Quantitative Comparison of Raman Activities, SERS Activities, and SERS Enhancement Factors of Organothiols: Implication to Chemical Enhancement*. *The Journal of Physical Chemistry Letters*, 2012. **3**(5): p. 560-565.
37. Mesophotonics. Available from: <http://www.mesophotonics.com/products/klarite.html>.
38. Japan, S.; Available from: <http://www.stjapan.de/en/shop/accessories-for-spectroscopy-microanalysis/raman-sers-substrate/>
39. Inc., S.; Available from: <https://www.stellarnet.us/spectrometers-accessories/sers-substrates/>.
40. Dolan, J.A., et al., *Gyroid Optical Metamaterials: Calculating the Effective Permittivity of Multidomain Samples*. *ACS Photonics*, 2016. **3**(10): p. 1888-1896.
41. Kahyun, H., et al., *Three-Dimensionally Isotropic Negative Refractive Index Materials from Block Copolymer Self-Assembled Chiral Gyroid Networks*. *Angewandte Chemie International Edition*, 2011. **50**(50): p. 11985-11989.
42. Hess, O., et al., *Active nanoplasmonic metamaterials*. *Nature Materials*, 2012. **11**: p. 573.
43. *Universal metal finishing guidebook*. Metal finishing. 2014, New York: Elsevier.
44. C Estrine, E., et al., *Mechanism and Stability Study of Gold Electrodeposition from Thiosulfate-Sulfite Solution*. Vol. 161. 2014. 687-696.