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Photonic Stopband Tuning in Metallo-Dielectric Photonic Crystals

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One of the most appealing aspects of photonic crystal structures is the photonic bandgap created in structures with sufficiently high dielectric contrasts between constituent materials. Periodic structures with a modest dielectric contrast between high and low index regions instead form a photonic stopband; the photonic stopband is linked to the principal diffraction resonance from the (111) crystal plane in the photonic crystal. Understanding how specific photonic crystal structures and their associated stopband positions can selectively interfere with incoming light is vital for implementing these structured dielectrics in a range of optical applications. Among the many methods existing to modify the signature optical response of photonic crystal materials, metallo-dielectric photonic crystals act to incorporate metal particles into the ordered arrangement of these structures. We examined the optical changes to the transmission spectrum resulting from copper, nickel and gold metal infiltration into polystyrene opals and TiO2 inverse opals. We report a consistent and interesting optical phenomena directly associated with the creation of metallo-dielectric photonic crystal structures. More pronounced and numerous diffraction resonances emerge in opal photonic crystals with a metal deposited across the top layer. Common to both opal and inverse opal structures, was a blue-shift in the position of the (111) photonic stopband which increased in magnitude with greater metal content in the structure. We investigate the origin of the photonic stopband blue-shift by variation of the metal content and the placement of metal in the photonic crystal structure. Our results suggest that metal introduced to structured dielectric media acts to tune the position of the photonic stopband by slight alterations to the effective dielectric constant or effective refractive index of the photonic crystal material.

The ability to direct and control light propagating through a medium is an essential criterion when designing an optical material. Inherently, photonic crystal materials possess a structural control over certain frequency ranges of electromagnetic radiation incident on the ordered layers of the material. From the first suggestions of photonic crystal materials as alternating dielectric layers,1,2 there has been significant interest in understanding and application of the optical control offered by photonic crystal structures.1–6 Of particular interest is the photonic bandgap established in these structures. Depending on the desired optical response, photonic structures can be designed and modelled as 1D,7,8 2D9,10 or 3D11–13 dielectric contrast materials. For 3D structures, yablokonite,14 artificial opals and inverse opals15 are all examples of photonic crystal materials. Photonic bandgaps can be engineered in both wavelength position and width of the depletion zone through control over the structural size or dielectric contrast of the material.15–17 A high dielectric contrast or difference between constituent materials of the photonic crystal medium is necessary for achieving a full, omnidirectional photonic bandgap.15,18 Materials with an inadequate dielectric contrast still exhibit a partial reduction of light intensity in the frequency range of the photonic bandgap. These incomplete photonic bandgaps are often referred to as pseudo-photonic bandgaps or photonic stopbands.19–21

The threshold for achieving a complete photonic bandgap is relatively large considering the dielectric constants of available materials. Artificial opal structures are generally consisting of spherical particles stacked and embedded in air medium; typical examples include spheres of polystyrene (PS), poly-methyl methacrylate (PMMA) and silica.22–25 These low dielectric materials form a low dielectric contrast vs the air background, generally yielding a pseudo-photonic bandgap.19,24 Metal oxides with a high dielectric contrast vs an air background are popular choices for inverse opal materials.26–28 Critically, the magnitude of the dielectric contrast (or refractive index contrast) will determine the appearance and width of the photonic bandgap for a given arrangement of material. Simulations of photonic bandgaps predict the appearance of an omnidirectional bandgap in an inverse opal structure for a refractive index contrast of 2.8 or greater,29,30 difficult to achieve with many metal oxide materials.

Even in the absence of an omnidirectional bandgap, photonic crystal structures have found a wide variety of applications, utilising both the easy to achieve structural order of materials and the presence of the stopband. Structurally ordering materials into a photonic crystal arrangement creates a porous material with higher levels of exposed surfaces compared to bulk arrangements. Higher surface areas are ideal for electrochemical31–33 and catalytic34–36 applications, where inverse opal structures have been applied for improved material performances. The sensitivity associated with the wavelength position of the photonic stopband has created numerous applications for both artificial opal and inverse opal materials. Shifts in the position of the photonic stopband can elucidate changes made to the material environment. Modifications to the periodicity or dielectric contrast of the system induce changes to the wavelength position of the photonic stopband; hence, photonic crystal materials are popular choices as optical sensors.37,38 A range of medical39–41 and biological42,43 research has successfully utilised the optical stopband of photonic crystals as sensors for detecting a variety of different substances. The optics of the ordered structures are not limited to just detection; the presence of an optical stopband across controllable wavelength regimes is ideal for creating optical waveguides.47,48 Light confinement by the dielectric contrast of the material structure has been used to develop optical cavities which have been applied as optical gain regions in lasing materials.48,49 Other spectral features associated with these materials, such as the slow photon effect50–52 at the edge of the optical bandgap region, can also be exploited to improve material performance in photocatalytic applications.52,53

There have been numerous studies characterising the properties of ordered material structures and their effects on the signature optical response of the photonic stopband.54–57 Choice of material

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dielectric constant for both high and low-index regions, $55 \pm 59$, angle of incidence, $50 \pm 62$, periodicity, $50 \pm 62$, structural anisotropy $63 \pm 64$, and liquid infiltration into the voids. $56,61,65$ are just some of the parameters which influence the optical behaviour of the structure. An interesting subclass of photonic materials are metallo-dielectric photonic crystals, where a modification of the base photonic crystal is accomplished through incorporation of a metal into the structure. It was initially proposed that the addition of metals into the photonic crystal structure should broaden the photonic bandgap due to the increase in the dielectric contrast of the composite material. $66,67$ At energies below the plasma frequency of a particular metal, the real part of the dielectric constant of that metal is negative; replacing some of the air in photonic crystal with a metal was expected to broaden the dielectric contrast between materials in the structure. Considering the geometry of the photonic crystal material, there are numerous methods of hosting metals in the ordered structure; material can be deposited on a metal layer, the top surface of the photonic crystal can be coated and a complete or partial infilling of the structural voids with metal are all possibilities. $68$ Metallo-dielectric structures have been predicted to introduce some interesting optical behaviour to the photonic band structures of these materials. $69 - 71$ For a metal film deposited on an opal template, it has been suggested that an optical cavity can form; higher amounts of reflections from the opal-metal interface increase the optical path length and can accentuate the appearance of diffraction resonances from lower index planes (non [111] planes) on the optical spectrum compared to an uncoated material. $68$ Interestingly, there have been some reports of a blue-shift in the wavelength position of the (111) diffraction stopband arising from metal insertion into the opal structure. $67,68,72$ The general assumption of the origin behind this blue-shift in the photonic stopband is a reduction in the effective dielectric constant or refractive index of the photonic crystal structure. $67,72,74,75$

Here, we present an investigation into the structural and optical evolution of Cu, Au and Ni metal-coated photonic crystal structures. Metals are deposited directly on the surface of PS colloidal opals and TiO$_2$ inverse opal structures via physical vapour deposition. Microscopy analysis of the metallised surfaces are used to characterise the appearance and deposition pattern of the metal films. Several thicknesses of metal coatings are deposited on photonic crystals surfaces and the consistency and growth of the metal film on surface features are assessed. Changes to the optical transmission spectrum upon addition of a metal film is tracked for several film thicknesses and different metals. Principally, a blue-shift in the (111) diffraction stopband is detected and tracked for each metal deposited on the surface of the PhC. The magnitude of the blue-shift is monitored relative to the thickness of the metal film on the surface, with more pronounced wavelength shifts reported for thicker films. Both PS opals and TiO$_2$ inverse opals are shown to demonstrate a blue-shift in the main diffraction stopband upon addition of a metal. These observations support previous assertions that metals in photonic crystal structures act to enhance the dielectric contrast between materials and induce a reduction in the effective dielectric constant of the material. Crucially, the dielectric contrast of the metal material infilling the structure is shown to be necessary for the blue-shift in the case of Cu, where partial oxidation of the metal to a metal oxide is demonstrated to decrease the magnitude of the blue-shift. Our results show that even a moderate modification to the surface of an opal or inverse opal structure with a metal is sufficient to induce a non-trivial change in the signature optical response of the photonic crystal material. We attempt to quantify the magnitude of the spectral blue-shift with film thickness and relate the impact of the negative dielectric metal on the average refractive index of the overall structure.

Experimental

**Pre-treatment and preparation of substrates.**—A transparent and conductive substrate was used for template formation, ideal for both optical measurements and microscopy examination. Fluorine-doped tin oxide (FTO) coated soda-lime glass substrates were purchased from Solaronix SA and were used for in the formation of all samples in this work. The breakdown of the conductive coating can be described by a thin layer ($\sim$20 nm) of FTO, deposited on a thin layer ($\sim$20 nm) of SiO$_2$, all deposited on a final thicker layer ($\sim$300 nm) of FTO on a glass substrate. The substrate glass was 2.2 mm thick and larger pieces were cut to make sample surface areas of $10 \times 25$ mm$^2$. Glass substrates were cleaned via successive sonication for 10 min in acetone (reagent grade; 99.5% Sigma Aldrich), isopropyl alcohol (reagent grade; 99.5% Sigma Aldrich) and de-ionised water. Cleaned sample surfaces were allowed to dry at room temperature. On the conductive side of the glass substrates, sample areas of $10 \times 10$ mm$^2$ were formed using Kapton tape to cover the remainder of the glass surface; both the front and back of the glass surface was covered with Kapton tape to promote the formation of colloidal crystals on the conductive $10 \times 10$ mm$^2$ sample area only. A Novascan PSD Pro Series digital UV-ozone system was used to pre-treat glass substrates and improve the hydrophilicity of the surface for colloidal crystal template formation.

Immediately prior to dip-coating procedure, prepared and cleaned sample surfaces were pre-treated by UV-ozone cleaning for 1 h.

**TiO$_2$ inverse opal formation.**—TiO$_2$ inverse opals were fabricated using PS opal samples as templates using the well-known sol-gel synthesis technique. $25,33,62,65,73$ Opal sphere templates were infiltrated with liquid (sol) precursor and the air voids in the opal photonic crystal were filled with the precursor. Ambient moisture reacts with the precursor in the opal structure and material (gel) forms in the interstitial voids which can be crystallised at high temperatures. For TiO$_2$ inverse opals, a 0.1 M TiCl$_4$ solution in isopropl alcohol was used as the precursor. An adequate amount of the precursor, enough to sufficiently wet the entire surface, was drop-cast onto the PS opal templates. The PS opal templates in the structure were removed via calcination in air at 450 °C with a ramp rate of 5 °C min$^{-1}$. The high temperature also allowed for the crystallisation of the TiO$_2$ material to crystalline anatase phase TiO$_2$. A titanium (IV) chloride tetrahydrofuran complex (TiCl$_4$·2THF 97%; Sigma Aldrich) was used as the source of TiCl$_4$.

**Formation of metal-coated photonic crystals.**—Metal films on the surfaces of photonic crystals were formed via physical vacuum deposition, specifically, magnetron sputter coating with a Quorum 150 T S magnetron sputtering system. Removable metal disc targets of thickness 0.1 mm and diameter 57 mm were used for copper, gold,
and nickel deposition. All targets were purchased from Ted Pella Inc. and featured a material purity of 99.99% for each metal. A film thickness monitor was used to deposit thicker metal coats onto surfaces; microscopy measurements were used to determine the actual thickness of the metal deposit formed due to the curved surfaces of photonic crystals. All metals were sputtered under an inert gas of high purity to ensure that the gas molecules did not react with the sputtered metal particles. Argon gas (>99.995% purity) was used as the sputtering gas in all cases. A target shutter in the sputter coater assembly allowed for cleaning of the target surface prior to film deposition, particularly important in the case of oxidising metal targets.

**Optical transmission analysis.**—Optical transmission spectra were recorded using an Ocean Optics Inc. UV–visible spectrometer (USB2000 + VIS-NIR-ES) with an operational range of 350–2200 nm. A tungsten-halogen lamp purchased from Thorlabs Inc. operating over the wavelength range 400–2200 nm was used as the unpolared excitation source. The angle of incidence between the normal of the photonic crystal surface and the incident light was fixed at 0° for all measurements. For the transmission spectra measured for each material, 100% transmittance was normalised to the transmission of a clean blank piece of FTO. Unless otherwise stated, the transmission spectra of all metal coated samples were recorded immediately after the coating procedure to minimise oxidation effects. To minimise spectral variance across samples, particularly in the case of pre and post-coated metal surfaces, spectra shown for a particular sample depict the features present (namely the position of the photonic stopband) across an average of 10 separate transmission spectra taken in close proximity on the sample surface. This process of determining an average photonic stopband position across an average of 10 separate measurements were obtained in several directions across the surface and used to assess the consistency of the metal coating on the photonic crystal structure.

**Results and Discussion**

**Metallo-dielectric copper-coated polystyrene opal photonic crystals.**—To assess the optical response associated with these metallo-dielectric photonic crystals, we first characterised the Cu shell formed on the surface of the PS opal photonic crystals. The thickness of the Cu film was controlled by varying deposition time during sputtering and correlating SEM thickness and metal film morphology with the values from the quartz crystal monitor.

Figure 1a shows a schematic diagram that depicts the shape of the metal layer formed on the top surface of the opal. From a top-down 2D perspective, as would be observed on a conventional SEM image, the circular top shape of the PS sphere is gradually converted to a hexagonal shell with increasing metal content. The hexagonally shaped metal shell should fit like a cap on top of the spherical opal. For an ordered FCC packed opal structure, the top layer should feature spherical PS spheres in point contact with one another as expected from the (111) planar geometry. As the mount of deposited metal increases during sputtering, from a 2D perspective, the hexagonally shaped metal layer expands into the interstitial air voids of the metallo-dielectric photonic crystal structure. In this scenario, point contacts between neighbouring spheres are converted to linear contact regions between neighbouring metal shells. With the metal layer overlaid on the top of the initial opal template, as in Fig. 1a, images of the metal-coated structure can be used estimate both the initial opal diameter ($D_{sphere}$) and the diameter of the metal coating on the surface ($D_{shell}$, measured from opposing hexagonal vertices).

Figure 1b displays SEM images depicting the geometric changes to the top surface layer of the opal when a Cu metal layer is deposited. The SEM images confirm the appearance of the metal-modified
structure as posited from the schematic in Fig. 1a. The spherical shape of the PS sphere is converted to a hexagonal shape when coated even with a moderate thickness metal layer. A metal layer of just 12 nm thickness atop a 386 nm PS opal is seen to sufficiently alter the geometry of the all the spheres in the top layer of the opal. The metal coating on the surface of the structure is found primarily on the top hemisphere of each sphere. The SEM image in Fig. 1c displays a side profile of Cu metal coated onto a PS opal. Even from a side profile, the preferential coating of the top surface with metal is observed. Opal layers beneath the top surface do not feature a complete conformal metal coating of Cu.

Figure 1d illustrates the method used to calculate the average metal layer thickness deposited across the opal surface. Diameter size distributions were constructed from the SEM images of the metallo-dielectric structures. Several hundred diameter measurements were made across multiple SEM images of the sample surface for both $D_{\text{sphere}}$ and $D_{\text{shell}}$. Thus type of approach allows a mean value for each diameter to be calculated and also assesses any potential asymmetry in the metal coatings. A mean diameter is useful for optical analysis where the periodicity of the structure is vital for predicting the optical response of the photonic stopband. More details on the measurements of $D_{\text{sphere}}$ and $D_{\text{shell}}$ for Cu metal coatings of various thicknesses can be found in the Supplementary Materials Fig. S2. From these size distributions, Cu metal layers of 2.5, 8, 12 and 15 nm were calculated to be deposited on opal surfaces. The appearance of the Cu metal layer on the surface of the opal with various different layer thicknesses can also be found in the Supplementary Materials Fig. S3. With increasing metal film thickness, there is a visible reduction in the interstitial area occupied by air in the structure. As the metal layer expands on the opal surface the interstitial area is reduced accordingly, and determined to be proportional to the thickness of the metal coating. The Supplementary Materials Fig. S4 characterises this reduction in interstitial area, as observed from SEM images, for each thickness of the Cu metal layers deposited on an opal surface. Figure S5 in the Supplementary Materials shows further SEM characterisation at low magnifications. Moderate cracks/defects across the photonic crystal surface can be seen from the SEM images. To accommodate for any spectral variance caused by structural non-uniformity, all stopband positions recorded were average across 10 sample sites on the surface, as described in Fig. S1. Large-area, crack-free opal template preparation methods may offer higher uniformity and eliminate the need for this averaging process in future works.

Analysis of the SEM images of metal coated opals is useful for providing a quantitative basis for assessing the amount of metal deposited on the surface as the metal layer thickness increases. Next, the optical effects of Cu metal deposited on the surface of an opal photonic crystal is assessed. The spectral response of the Cu metal film atop the opal surface can be interpreted relative to the uncoated opal in terms of a reduction in the overall transmission of the modified photonic crystal structure. The reduction in transmission, the appearance of further diffraction resonances and the blue-shift of the principal optical stopband become more prominent with increasing metal layer thickness. These effects associated with increasing metal content in the photonic crystal structure are presented in Fig. 2.

Figure 2a displays the transmission spectrum associated with a flat Cu metal film on FTO-coated glass deposited under the same conditions used to form a 15 nm Cu metal layer on an opal surface. The substantial attenuation of the light intensity, seen as a significant drop in the transmission intensity, is as expected for a highly reflective metal film on a surface. For thin films of Cu metal, the transmission maximum at approximately 570 nm and slight transmission minimum at approximately 760 nm have been previously attributed to interband photon transitions for fully filled d-shells and a localised plasmon effect depending on the thickness of the film,
The high reflectivity of the metal coating results in the decreasing transmittance of metal coated opal structures with increasing metal layer thicknesses. This trend can be observed in Figs. 2b, 2c, 2e and 2f where the light intensity observed in transmission is strongly attenuated with increasing Cu layer thickness. From these optical transmission spectra, the appearance of non [111] diffraction resonances from the opal structure become much more pronounced with the addition of a Cu metal layer over the top surface of the opal. This is particularly apparent in Figs. 2e and 2f where the thickest Cu metal layers are deposited. For thicker metal layers, 4 diffraction resonances become prominent transmission dips in comparison with the uncoated opal sample. It has been previously proposed that the emergence of non [111] diffraction resonances in metal-coated opal structures can be attributed to the formation of an optical cavity, enhancing the relative intensity of higher energy resonances compared to the overall transmission of the photonic crystal. This explanation seems plausible in our case, where significant spectral features emerge at the high energy side of the principal (111) diffraction stopband.

The wavelength position for the transmission minimum ($\lambda_{\text{min}}$) associated with diffraction from a crystal plane of indices hkl can be calculated from the Bragg-Snell relation as follows:

$$\lambda_{\text{min}} = 2d_{\text{hkl}} n_{\text{eff}}$$

Referring to Eq. 1, $d_{\text{hkl}}$ is the associated interplanar spacing of the crystal plane, $n_{\text{eff}}$ is the effective refractive index of the photonic crystal structure and $\theta$ is the angle of incidence between the normal to the crystal plane and the incident light. For the spectra presented in Fig. 2, some simplifications to Eq. 1 can be made by assuming a first order resonance ($m = 1$) and normal incidence ($\theta = 0^\circ$) of the incoming light. For these conditions the Bragg-Snell relation for the (111) diffraction plane becomes:

$$\lambda_{111} = 2d_{111} n_{\text{eff}}$$

For an FCC structure, as anticipated from an artificial opal template, the interplanar spacing ($d_{111}$) of the (111) plane can be determined using the centre-to-centre (D) distance between opals in the structure are follows:

$$d_{111} = \sqrt{\frac{2}{3}} D$$

The effective refractive index for a composite structure, such as a photonic crystal medium, can be estimated using a number of different methods. For an artificial opal template consisting of materials with high ($n_1$) and low ($n_2$) refractive indices in respective volume fractions $\phi_1$ and $\phi_2$, the effective refractive index can be calculated as:

$$n_{\text{eff}} = n_1 \phi_1 + n_2 \phi_2$$

Thus, the wavelength position of the principal (111) diffraction stopband in an uncoated FCC PS ($\phi = 1.57$ at 900 nm, $\phi = 0.74$) opal in an air background ($\phi = 1$, $\phi = 0.26$) can be determined from knowledge of the centre-to-centre diameter as follows:

$$\lambda_{111} = 2.84 \sqrt{\frac{2}{3}} D$$

The mean centre-to-centre distances, as calculated from the size distributions for each sample, are adopted here as an estimate of the average D for each opal sample. For the uncoated opal samples presented in Figs. 2b, 2c, 2e and 2f the mean centre distances were calculated as 394, 386, 386 and 393 nm, respectively. Estimating the position of the principal (111) transmission stopband using Eq. 5 yields wavelength position estimates of 913, 895, 895 and 911 nm, respectively. These estimates show a relatively strong agreement with the experimentally determined stopband positions of 875, 875, 885 and 888 nm, shown in Figs. 2b, 2c, 2e and 2f, respectively. The metallo-dielectric opals in these spectra all display a blue-shift in the position of the photonic stopband, and the magnitude of the blue-shift increases for thicker Cu layer deposits. In the case of the Cu-coated opal spectra, shown in blue in Figs. 2h, 2c, 2f and 2f, the central wavelengths of the shifted photonic stopbands are now located at 870, 857, 862 and 860 nm, respectively. The application of a conformal Cu metal coating to the top layer of the optical surface with layer thicknesses of 2.5, 8, 12 and 15 nm induced a blue-shift in the photonic stopband of 3, 18, 23 and 28 nm, respectively. Figure 2c displays this relation graphically, where a thicker Cu metal layer is shown to induce a greater shift in the photonic stopband, in general. Similar results are reported for Ni-coated opals, characterised in the Supplementary Materials Figs. S6 and S7; thicker Ni metal layers induce a greater stopband blue-shift. In the proceeding sections the existence of this blue-shift is investigated for other metals and photonic crystal structures with a mechanism proposed for its origin.

**Metallo-dielectric Cu, Au and Ni-coated opal and inverse opal structures.**—By variation of the metal coating material and the type of photonic crystal surface, the optical effects of metal infiltration into a dielectric medium are further investigated, specifically focusing on any changes to the position of the principal (111) photonic stopband. The optical effects of metal coatings of Cu, Au and Ni on both PS opal templates and TiO$_2$ inverse opals are assessed here. First starting with the coated PS opal structures, Figs. 3a–3c show the optical transmission spectra for Cu, Ni and Au metal coatings deposited on the top surface of the opal, alongside SEM images of the coated structure. The thicknesses of the metal layers deposited were determined from SEM analysis using the same process described in Fig. 1. More detailed analysis of the SEM images and size distribution data for the Ni and Au coated PS opals can be found in the Supplementary Materials Figs. S8 and S9. Metal layers of Cu, Ni and Au were found to be deposited at thicknesses of 12, 9 and 5.5 nm. For all metals, a complete surface coating of the opal is formed and from the SEM images the metal shell creates the 2-D hexagonal pattern as discussed for the Cu metal. Figures 3a–3c also show higher magnification SEM images for the Cu, Ni and Au metal layers. Similar sized metal nanoparticles are found in the Cu and Ni films (~5–8 nm) with slightly larger metal nanoparticles found for the Au film (~10–15 nm).

The optical transmission spectra for uncoated PS opals and metal-coated opals are also shown for Cu, Ni and Au layers in Figs. 3a–3c, with the spectral appearance of a flat metal film shown underneath the plot. The high reflectance of the metal films in the visible spectrum can be seen from the flat films deposited on the glass surface, with low transmission intensity through the films. The Au metal film displays the highest transmission intensity, presumably due to it being the thinnest deposit of metal on the surface. In the case of the 12 nm thick Cu-coated opal, the position of the photonic stopband has already been discussed in the previous section. The uncoated opal used in the deposition of Cu metal displays a photonic stopband at 885 nm, close to the predicted position of 895 nm from Eq. 5 using a mean diameter of 386 nm. The mean diameters for the uncoated opal in the case of the Ni and Au deposition, as calculated from SEM analysis and size distributions in Supplementary Materials Fig. S9, were calculated as 376 and 372 nm respectively. The predicted wavelengths of the photonic stopbands for Ni and Au uncoated opals, as per Eq. 5, are calculated as 872 and 863 nm. From the transmission spectra in Figs. 3b and 3c, there is a reasonable agreement between these calculated positions and the experimentally observed stopbands at 896 and 897 nm for the uncoated opals used for Ni and Au deposition.

With a Cu layer of 12 nm deposited on the opal surface, we measured a blue-shift of the principal (111) diffraction stopband from 885 nm to 862 nm after metallization. Similarly, this stopband...
blue-shifting is observed with the addition of both Ni and Au metal. For a nominal Ni metal layer thickness of 9 nm, the photonic stopband shifts from 896 nm to 878 nm. Even a thin 5.5 nm metal layer of Au induces a moderate stopband blue-shift of 15 nm, from 897 to 882 nm. In all instances, metal deposited on the opal surface is demonstrated to induce a blue-shift of the (111) diffraction stopband with a significant reduction in transmission intensity and the emergence of higher energy cavity resonances.

We also examined the blue-shift phenomenon with metallo-dielectric photonic crystal fabrication with the inverse opal geometry using Cu, Ni and Au metals. The deposition rates and times used in the formation of the metal coats were identical to the parameters used to coat opal surfaces in Fig. 3. The structure of the IO is inherently different to the parent opal template; TiO2 IOs consist of low dielectric air spheres ($\phi = 0.74$) surrounded by a network of high dielectric TiO2 material ($\phi = 0.26$), with a specific overall effective refractive index. With a metal deposited onto an IO material, it stands to reason that the metal can penetrate deeper into the material compared to an opal structure due to the highly porous IO structural geometry.

The effects of Cu, Ni and Au metal deposition onto a TiO2 IO surface can be seen in Fig. 4. The surface of a typical TiO2 IO can be seen in the SEM image in Fig. 4a, showing the ordered macroporous IO structure formed from inverting the planar (111) PS opal crystal plane. The mean pore size associated with TiO2 IOs, as measured from size distribution data shown in the Supplementary Materials Fig. S10, is calculated to be 440 nm. Previous studies of the optical characteristics of TiO2 IOs of similar dimensions have indicated the presence of an optical stopband located at ∼700 nm. The transmission spectra for the uncoated TiO2 IOs shown in Figs. 4b–4d feature optical stopbands located at 687, 709 and 702 nm, respectively; the position of the photonic stopband is relatively consistent for similarly sized material pores.

The SEM images in Figs. 4b–4d for TiO2 IOs coated with Cu, Au and Ni show the effects of the metal deposition on the IO structure. The thin walls (∼12 nm) of TiO2 material on the top surface become...
thicker (45, 32, and 35 nm for Cu, Au and Ni, respectively) as metal deposits over the structure. The deposited metal can also be seen to coat beneath the top surface with metal particles clearly visible on layers below the surface. The SEM images support the assumption that the sputtered metal particles can penetrate further into the porous IO material and incorporate into the structure beyond the top surface. Additional SEM images of metal coated TiO2 IOs can be found in the Supplementary Materials Fig. S11 for further characterisation of the modified structure.

The positions of the photonic stopbands for Cu, Au and Ni metallo-dielectric TiO2 IOs can also be seen from the transmission spectra presented in Figs. 4b–4d. Similar to the metal-coated opal structures, the position of the photonic stopband is blue-shifted to some extent for every TiO2 IO modified with a metal deposit. In the case of the Cu-coated TiO2 IO, there is significant shift in the stopband position to higher energy (from 687 nm to 651 nm, a blue-shift of 36 nm) when metallised with Cu. The photonic stopband is clearly visible for the Cu-coated TiO2 IO. In contrast, the photonic stopband for the Au-coated TiO2 IO is more difficult to observe on the transmission spectrum, due to partial overlap of the broad transmission maximum observed for Au films with the shifted stopband in this case. The small transmission dip observed at 662 nm is most probably the location of the shifted stopband for the Au-coated TiO2 IO, constituting a significant blue-shift of 40 nm. The Ni-coated TiO2 IO exhibits the smallest shift in photonic stopband position, shifting from 709 nm to just 701 nm, a blue-shift of 8 nm.

The magnitude of the larger blue-shifts observed in both Cu and Au could be explained by the plasmonic properties of these metals and the injection of hot electrons from Cu and Au into TiO2; hot electron effects are known to enhance the photocatalytic properties of semiconductors such as TiO2. Local surface-plasmon resonances arising from metal nanoparticles embedded into TiO2 films have been shown to alter the transmission properties of the TiO2 film. It is unclear from the dataset presented here whether overlapping these changes to the transmission with the photonic stopband effect would influence the position of the stopband. For Cu and Ni metallo-dielectric IOs the shape and relative depth of the photonic stopband is retained upon metal deposition. For the Au layer, the relative intensity of the stopband is diminished, possibly due to the overlap with the local surface-plasmon resonances. Nevertheless, in all cases of metal incorporation into IO structures, a blue-shift of the photonic stopband is observed. This blue-shift persists in both opals and IOs in spite of the inverse porous structure and energies of their characteristic stopbands. We next attempt to account for this shifting of the photonic stopband by analysing the influence of metal type and its placement in the structure.

**The significance of metal particles for the photonic stopband blue-shift.**—Having observed a blue-shift in the photonic stopband position for all photonic crystal structures coated with a metal layer, the significance of the metal inclusion in the structure is next explored. Cu metal is known to oxidise slowly at room temperature to form copper oxides; the oxidation process is continuous with
dominant Cu-O and minor CuO phases of oxidised copper formed. In the case of metallo-dielectric photonic crystals, this oxidation process can be leveraged to investigate how the metal specifically alters the optical properties of the structure. The oxidation of the metal over time effectively removes a certain percentage of metal material as it is replaced with an oxide of the metal. The position of the photonic stopband for photonic crystal structures is susceptible to slight variations between similarly sized structures; this can be observed even examining the data presented in Fig. 1, where the positions of the principal photonic stopband fluctuated slightly for similarly sized opal templates. An oxidation of Cu metal on the surface of an opal template allows for a variable metal content to be examined on the exact same template, removing any possibility of potential stopband position fluctuations between different samples.

The process of Cu metal layer oxidation and the optical effects associated with oxidation of the metal can be seen in Fig. 5. Figure 5a schematically depicts the formation of a layer of copper oxide on the top surface of the metal layer after 1 week. We assume that some amount of the Cu metal is oxidised to various copper oxides after 1 week of exposure to an ambient atmosphere at room temperature. The accompanying SEM images of the surface of the metal-coated spheres appear to show an expanded and rougher surface after this 1-week oxidation period. Elemental composition analysis is presented in a table in Fig. 5e, showing the relative wt% of elements detected from EDX line scan measurements for 12 nm of Cu metal deposited over the surface of polystyrene spheres.

For the recently deposited Cu film, carbon and copper are present in highest abundance, as expected from copper metal sputtered over polystyrene (C₈H₈)n. Oxygen is present in this initial scan, in highest abundance, as expected from copper metal sputtered over Cu metal deposited over the surface of polystyrene spheres. The relative wt% of oxygen has almost doubled from 2.5% to 4.9%, suggesting a moderate oxidation of the copper film to various copper oxides, as expected.

The optical spectra of the Cu-modified PS opals, presented in Fig. 1, are examined following an oxidation period of 1 week in ambient atmosphere conditions. The spectra presented in Figs. 5b, 5c, 5f and 5g are obtained and compared for measurements made on recently metal-coated samples vs samples allowed to oxidise for 1 week. Slight increases in transmittance are observed for most samples, to be expected from the partial removal of reflective metal particles. Interestingly, in the case of the (111) photonic stopband we observe a consistent reduction in the magnitude of the blue-shift caused by a metal coating. A bar chart summarising these results can be seen in Fig. 5d, showing a reduction in the blue-shift (Δλ_min) of the stopband for every metal layer thickness after a period of 1 week. An overall blue-shift of the stopband, compared to the uncoated opal stopband position, is still observed for every sample after oxidation.

Similar oxidation analysis of Ni metal-coated polystyrene opals can be found in the Supplementary Materials Fig. S12 showing a slight reduction in the magnitude of the blue-shift, much like the Cu-coated opal templates. Copper-coated TiO₂ inverse opals were also examined after 1 week of oxidation, and detailed in the Supplementary Materials Fig. S13. The Cu-coated TiO₂ IO showed a dramatic reduction in the magnitude of the blue-shift from 36 nm to just 8 nm after 1 week of oxidation. It would appear that the specific properties of the metal (and not the metal oxide) are important for establishing potential stopband position, is still observed for every sample after oxidation.

Figure 5. (a) A schematic representation of copper oxide formation on the surface of Cu metal films over time. Transmission spectra showing a comparison between newly coated Cu metal layers and the same samples after 1 week in ambient atmosphere for (b) 2.5 nm Cu, (c) 8 nm Cu, (f) 12 nm Cu and (g) 15 nm Cu thicknesses. (d) Graphical representation of the magnitude of the stopband blue-shift (Δλ_min) for Cu layer thicknesses over time. (e) EDX elemental analysis showing the relative wt% of elements detected in a newly coated Cu metal layer over a PS opal template as compared to elemental analysis of the same sample taken after 1 week of exposure to ambient atmosphere conditions.
the blue-shift of the (111) photonic stopband in a metallo-dielectric photonic crystal.

The placement of the metal material in the opal structure also seems to be significant for inducing the blue-shift in the (111) photonic stopband. Figures 6a and 6b represent two methods in which metal material was placed in contact with PS opal photonic crystals. The scenario depicted in Fig. 6a has been discussed for materials presented in Figs. 1, 3 and 5: metal layers are deposited over the top surface of the opal photonic crystal by sputter deposition. In addition to a conformal metal coating on the top surface of the opal (see Fig. 6a), we confirm that some metal deposited onto the second layer through the interstitial voids on the top surface. The presence of metal on the second layer of opals was confirmed via EDX elemental composition analysis and line scan measurements of Ni, Au, and Cu-coated PS opals, as seen in the Supplementary Materials S14—S16. For Cu-coated opals, the elemental composition is compared on the same sample surface between a recently deposited (~20 min after film deposition) measurement and a scan taken after allowing for 1 week of oxidation of the Cu film under ambient atmosphere conditions. EDX measurements indicate the presence of reduced metal content, compared to the surface coating, in the interstitial voids atop the second layer of PS spheres. The EDX measurements for Ni also indicate a relatively uniform thickness for the Ni metal content deposited on the top surface.

Figures 6c and 6d summarise the observations made for PS opals coated with metal; a blue-shift of the (111) photonic stopband is observed for every metal investigated and the magnitude of the blue-shift increases with thicker metal layers, as seen with Cu metal. Figure 6b illustrates the scenario of a PS opal structure grown on a sputtered metal film. The bottom of the photonic crystal structure is in direct contact with the metal; the metal is not incorporated into the structural voids or layers of the opal template in this case. Optical spectra showing an opal prepared on an uncoated substrate vs a gold film-coated substrate, deposited with identical sputter coating settings to the gold film formed in Fig. 3c, can be seen in Fig. 6e. For consistency in the spectral analysis of the opal template, half of the substrate was coated with Au and the other half uncoated so that spectra could be taken from different areas of the same sample. Optically, a significant decrease in the transmission intensity for the Au-coated substrate is observed in Fig. 6e, as expected due to the high reflectivity of Au metal. The (111) photonic stopband, located at 905 nm for the uncoated substrate, displays no detectable blue-shift when opals were deposited on the Au-coated substrate vs the uncoated substrate. This contrasts with the 15 nm blue-shift observed for Au-metal deposited over the top surface of the opal. Metallization of the opal in the form of hemispheres, with some interstitial infilling, is necessary to invoke a stopband blue-shift; a planar gold film on one side of the opal photonic crystal slab has no effect, even when the metal is capable of supporting surface plasmon polaritons.

Regarding the blue-shift of the photonic stopband, we posit that the optical properties of the metal and its location in the dielectric medium are necessary considerations for causing a shift in the (111) stopband position. This blue-shift is detected for all metals (Cu, Ni and Au) tested and for both the artificial opal and inverse opal templates. Changes to the stopband position of a photonic crystal structure caused by changes in the interplanar spacing (d(111)) or changes to the effective refractive index of the structure (n_eff), as per Eq. 2. Changes to the interplanar spacing of an entire opal due to thin metal coating layers only on the top surface of the photonic crystal are unlikely to occur here. The weight of the thin metal coatings over the top surface (~1 μg assuming a 12 nm Cu layer over 1 cm²) are insufficient to induce axial compression on the [111] plane that would cause a compression throughout all the PS spheres, which would be required to shift the bandgap. Each individual layer of spheres is heavier (by a factor of 2 than the metal coating on the top surface). Second, any compression of the axis would need to be uniform and consistent, compressing each layer of spheres equally due to the metal, which is very unlikely as compression by a single layer of sphere in the absence of metal does not compression the underlying layers to cause any such shift. We believe the most likely explanation for this behaviour is a reduction in the effective dielectric constant or effective refractive index of the metallo-dielectric photonic crystal. Previous works with various metallo-dielectric structures have also assumed a reduced effective dielectric

Figure 6. Schematic diagrams depicting the proposed position of metal in metallo-dielectric structures prepared from (a) sputter deposition over the top surface of the opal and (b) opal template formation over a sputtered metal film on a glass substrate. The blue-shift (Δλ_min) in the stopband position for metal deposited over the surface of an opal is shown for transmission spectra and graphically in (c) and (d), respectively. (e) A transmission spectra comparison for opals prepared on an uncoated glass substrate vs a 5.5 nm Au metal film.
constant or effective refractive index.\textsuperscript{67,72,74,75} The plasma frequencies for Cu, Ni, and Au metal films are reported as energies in the UV range,\textsuperscript{86} with a negative real part of the dielectric function at energies below the plasma frequency. Metals at optical frequencies below the energy of the plasma frequency, would thus feature a negative dielectric constant. Incorporating a metal into a photonic crystal template should enhance the dielectric contrast of the material and reduce the effective dielectric constant of the composite material by replacing air in the structure with a negative dielectric material, and this occurs in the top surface region where the spheres are half-coated, and the interstices between spheres that are also metallized.

In terms of the (111) photonic stopband, this reduction in the effective dielectric contrast of the photonic crystal structure is most likely reflected as a decrease in the effective refractive index of the structure, resulting in a blue-shift of the stopband position per Eq. 2. With this assumption, more metal introduced into the structure would act to further decrease the effective refractive index while simultaneously increasing the magnitude of the blue-shift. The thin surface coatings of metals applied in fabricating our metallo-dielectric structures would only replace a small fraction of the air in the material, establishing small changes in the effective refractive index. Taking the 12 nm Cu layer, 9 nm Ni layer and 5.5 nm Au layer deposited on PS opals (see Fig. 3) as an example, the stopband shifts of 23, 18 and 15 nm would constitute minor changes to the effective refractive index from 1.422 to 1.385, 1.393 and 1.398, respectively. Based on our investigation of data, it would seem as if thin coatings of a negative dielectric metal are sufficient to induce minor changes in the effective refractive index of photonic crystal structures, subsequently inducing a blue-shift in the (111) photonic stopband position.

It is important to consider the role of plasmons in these structures. Extraordinary optical transmission from coupling of surface plasmons will only be observable for these structures at higher wavelengths (beyond our measurement capability), if these modes are supported. The 3D photonic crystal (whether opal or inverse opal) defines the Bragg diffraction response and the stopband. With a hemispherical metallic coating on the top layer and partial, but periodic, infilling of the voids in the case of colloidal opals, coupling between a metalized 2D slab and the 3D photonic crystal is considered briefly. The higher energy oscillations observed here are also seen in metal coated 2D monolayer opal colloidal photonic crystals,\textsuperscript{67} and we also note a suppressed transmission caused by the larger imaginary component of the dielectric constant for Ni coated metallo-dielectric photonic crystals. However, observing these transmissions features in 3D opals is consistent with cavity modes. The metallization modifies the stopband in a unique manner (a blue-shift) even with an effective inverse in the periodicity of the dielectric constant in an inverse opal. Angle-resolved investigations using polarized light will likely be needed to determine any plasmonic coupling (Bragg and Mie plasmons) and a wider spectral range is necessary to confirm EOT effects or Fano resonances in metal-coated metallo-dielectric photonic crystals. The fact that we see this response for the first time in a metal-coated inverse opal, consistent with the mechanism that allows for these observations in colloidal opal photonic crystals, provides opportunities for investigations and applications in photocatalysis, spectrophotocatalytic supports, and surface-enhanced scattering spectroscopy to name a few.

Conclusions

The optical effects of metallo-dielectric photonic crystals have been investigated for a variety of different metals and structured dielectric materials. Simple metal surface coatings applied to both opal and IO templates were demonstrated to significantly alter the optical spectrum of the material in terms of the transmitted light intensity, the appearance of several diffraction resonances and a consistent shift in the position of the photonic stopband. Analysis of the various metallo-dielectric photonic crystals presented show that the thickness of the metal layer, the negative dielectric properties of the metal and the placement of the metal deposit in relation to the ordered structure are all essential considerations in predicting the optical changes to the modified system. Knowledge of these parameters should allow for a tuneable response to the optical spectrum of a metal-modified dielectric medium.

For Cu, Ni and Au metal deposited over the top surface of PS sphere opal templates, persistent blue-shifts in the photonic stopband position were recorded relative to uncoated PS sphere templates. Thicker metal coatings were correlated with increased magnitudes of the blue-shift in Cu metal. Expanding our analysis to investigate metal infiltration into innately different structured materials, the TiO\textsubscript{2} inverse opal, presented a corresponding blue-shift of the photonic stopband found in IO structures modified with Cu, Ni and Au. In TiO\textsubscript{2} IOs, stronger stopband shifts were observed for Cu and Au metal deposits compared to Ni, with possible hot electron generation altering the optical properties of the semiconductor. Nevertheless, a blue-shift of the photonic stopband position of some magnitude was observed for every metal deposited and incorporated into the structure of PS sphere opal and TiO\textsubscript{2} IO photonic crystals.

Through oxidation of the Cu metal, it was demonstrated that the specific properties of the metal material were necessary for the reported (111) stopband blue-shift. Oxidation of the Cu metal to various copper oxides decreased the reported magnitude of the blue-shift. Forming metallic hemispheres as the opal top coating is necessary to induce a stopband spectral blue-shift. By formation of the PS opal template on a Au-coated substrate and the subsequent detection of no stopband blue-shift, the placement of metal material directly into the photonic crystal material medium was linked to the origin of the spectral blue-shift. The consistent (111) photonic stopband blue-shift found using all metals used in this work is most plausibly explained by a reduction in the effective refractive index of the metallo-dielectric photonic crystal. This long-standing assumption has been presumed and attributed to observed spectral shifts in other works.\textsuperscript{67,72,74,75} With the results and evidence presented here, a strong argument can be made for clarification and association of the origin of the photonic stopband blue-shift in metallo-dielectric structures with a reduction in the effective refractive index of the composite structure. We posit that the inclusion of a negative dielectric metal in a photonic crystal structure is not only sufficient to increase dielectric contrast in the material, as was proposed in initial reports of metallo-dielectric structures,\textsuperscript{65,67} but also to tune the effective dielectric constant or effective refractive index of the dielectric medium. Our results would indicate that even thin surface coats of the photonic crystal structure are capable of moderate modifications to the effective refractive index of the system, dictating the consistently observed stopband blue-shift with metal infiltration into the structure.

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