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Switchable Plasmonic Metasurfaces with High Chromaticity Containing Only Abundant Metals

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Abstract

Plasmonic color generation offers several advantages but is also limited by the cost and availability of noble metals like gold. In this work we present color-tuneable metasurfaces with high chromaticity and reflectivity consisting of an aluminum mirror, a dielectric spacer and a plasmonic nanohole array in copper. Copper is shown to be an excellent alternative to gold when properly protected from oxidation and makes it possible to generate a wide RGB gamut covering 27% of the standard RGB. By patterning the metasurfaces into microscale pixel triplets, color photos can be well reproduced with high resolution over wafer-sized areas. Further, we demonstrate active modulation of the reflected intensity using an electrochromic conductive polymer deposited on top of the nanostructures by screen printing. This technology opens up for ultrathin and flexible reflective displays in full color, i.e. plasmonic electronic paper, compatible with large-scale sustainable production.

KEYWORDS: plasmons, colors, nanostructures, electrochromism, electronic paper

TOC graphic

Plasmonic nanostructures have been used to generate decorative colors for thousands of years.¹ Recently there has been a renowned interest in utilizing such strong light-matter interactions for color generation^{2, 3} and active electrochromic devices.^{4, 5} Some of the most prominent advantages of plasmonic coloration are that ultrathin nanostructures or “metasurfaces” are sufficient for high chromaticity and that the structures are generally more robust than organic dyes. Also, by nanofabrication techniques, plasmonic images can be produced at extremely high resolution.⁶⁻⁸ Furthermore, various techniques can be implemented in order to make the picture display dynamic.⁹ If a conductive polymer is grown on the plasmonic surface, electrochromic switching becomes possible and the colors are clearer than those generated by polymers alone.¹⁰ Using suitable nanostructures this technology opens up for reflective displays operating in color.¹¹

However, plasmonic devices are generally based on noble metals (mainly Au) which are rare and expensive. This limits potential applications and production of functional devices. Although little material is needed for ultrathin nanostructures in principle, much is lost in the fabrication process, especially since vacuum deposition techniques are almost always necessary. This has lately led to an intense focus on “sustainable plasmonics”, i.e. the use of abundant metals, in particular aluminum¹² (Al). Still, color generation with nanostructures based on Al has several limitations to date. The structures are often only prepared on small areas because of the serial nature of the nanolithography techniques used^{13, 14} and although the color range can be impressive considering that only one metal is used,¹⁵⁻¹⁷ there is still room to improve the chromaticity. Also, many devices have been designed for dark-field illumination¹³ (light scattering), but this configuration is more suitable for sensing applications¹⁸ rather than electrochromic devices. Further, the only implementation of active intensity modulation is liquid crystals above the nanostructures,⁴ which limits the overall reflectivity/transmittance due to the polarization

dependence and makes the pixels considerably thicker. This in turn makes the system unbendable as well as sensitive to the viewing angle. Naturally, many of these limitations apply also when noble metals are used for plasmonic color generation and in electrochromic devices.

In this work we present high chromaticity plasmonic metasurfaces based on a metal – insulator – nanohole array (MIN) thin film configuration containing only abundant metals. We evaluate the relatively unexplored¹⁹ metal copper (Cu) for plasmonic color generation and show that this can generate a much wider gamut compared to Al alone. The MIN structures show high reflectivity and can be patterned over wafer sized areas. Colorful pictures can be clearly reproduced at high resolution using red, green and blue pixel triplets. In addition, we show that an electrochromic polymer film can be prepared on the MIN structures by screen printing, which enables on/off switching of the colors without the need for polarizers. In simple prototypes we demonstrate that this technology can provide flexible reflective displays with ultralow power consumption and compatibility with large scale production due to solely cheap materials.

Motivated by the low price of Cu (comparable to Al) we started by characterizing the optical response of semitransparent Cu films containing short-range ordered nanoholes prepared by colloidal lithography.²⁰⁻²³ Plasmonic activity in Cu is relatively unexplored in the literature²⁴ because spontaneous oxidation normally causes too high damping,²⁵ although chemical modifications may provide stability at least for the timescale of the experiments.²⁶ Nanoholes in Cu have been prepared previously²⁷ but their optical response has to the best of our knowledge never been characterized, most likely due to the problem of oxidation. We protected the metal by an additional 20 nm alumina (Al_2O_3) coating (Fig. 1A) deposited in the same electron gun evaporator run, such that the Cu film is never exposed to air in between. This protection provided excellent long-term stability (in air) as verified by no significant changes in the optical properties

over the timescale of the study (~1 year). Due to the relatively similar permittivity of Au and Cu (when free from oxidation),²⁸ we expected the far field spectra to be comparable to structurally identical short-range ordered nanohole arrays prepared in semitransparent Au films (see literature).²⁰⁻²³ Indeed, the extinction spectra of nanoholes in a 30 nm Cu films (standard error ± 1 nm) showed the characteristic peak in the red, representing coupling to surface plasmons by the short-range ordering of the apertures (Fig. 1B),²⁰ followed by an enhanced transmission at nearby longer wavelengths (Fig. 1C). The resonance features are only slightly broadened compared to Au nanohole arrays.²⁰⁻²³ This can to some extent be attributed to the fact that in contrast to Au there is no need for an adhesion layer (Ti or Cr) under the Cu film on glass. Note that the colloidal lithography provides a saturated monolayer and that the number density of holes should not be reduced since it destroys the short-range ordering and consequently the plasmonic activity.²⁰ The resonances redshift with increasing the hole (colloid) diameter, which is due to the increased effective periodicity of the array. The hole diameter itself does not influence the resonance wavelength although larger holes give more scattering.²³ Furthermore, the resonances also redshift as the film thickness decreases to 20 nm (Fig. 1D) as predicted by the dispersion relation of the bonding surface plasmon mode in the finite film.^{20, 29}

Figure 1. Characterizing the optical response of short-range ordered nanohole arrays in semitransparent Cu films. (A) Schematic of the structure and description of the different hole arrays. (B) Electron microscopy image taken from above of a sample prepared with 158 nm colloids. (C) Extinction spectra of samples prepared with a 30 nm Cu film. (D) Extinction spectra of samples prepared with 20 nm Cu.

We hypothesized that it should be possible to use the (Al_2O_3 protected) Cu nanohole arrays with an Al mirror and a Al_2O_3 spacer to create MIN metasurfaces (Fig. 2A) with high chromaticity. As in our previous work with Au and Ag structures,¹¹ we utilize a combination of Fabry-Perot interference (cavity mode) and surface plasmons to generate high resonant polarization-insensitive

reflection. The highly reflective bottom 100 nm Al mirror has essentially zero transmission³⁰ and is covered by an Al₂O₃ film onto which the Cu nanohole arrays are prepared. By changing the Al₂O₃ layer thickness a wide color palette can be generated because the reflection from the cavity mode and the surface plasmon both change their individual resonance wavelengths due to coupling between the metal films. The plasmonic activity of the structure is vital since it causes resonant absorption and scattering of light, which strongly increases the color range compared to utilizing the cavity mode alone. This was obvious from the appearance of the same structures prepared without nanoholes in the Cu film, which showed weaker colors, especially for green and blue, regardless of Al₂O₃ thickness. By calculating the dispersion relation of surface plasmons in the MIN system using a generic method²⁹ we confirmed plasmon coupling in the yellow to red region when the Al₂O₃ thickness lies in the interval 50-150 nm (Supporting Information). We also evaluated MIN structures prepared with only Al (or Ag) but those colors were much poorer (example in Supporting Information), especially in the red. This is to some extent because of the contribution from interband absorption in Cu (or Au),^{24, 28} but also because the plasmons are excited at higher energies in Ag and Al.²²

Figure 2. Reflective metal – insulator – nanohole array metasurfaces. (A) Layout of the structure with Al as bottom mirror, variable Al_2O_3 spacer and a short-range ordered array of 158 nm nanoholes in a 20 nm Cu film (see also Fig. 1C). (B) Reflectivity spectra in air with incident light ranging from zero to 41° for the values of Al_2O_3 thickness that gives the best primaries. For red, there are no nanoholes in the Cu since this reduces the reflectivity (c.f. dashed spectrum). (C) CIE 1931 xy chromaticity space showing a comparison between the metasurfaces and standard RGB. (D) Photo of samples with the primary colors.

In order to optimize the colors of the Al/Cu MIN structures in more detail, we tested several different nanohole arrays as top layer while also varying the Al_2O_3 thickness by creating a gradient on the surface.³¹ Concerning the nanohole array, we found that good colors were achieved for $D = 158$ nm nanoholes in a $h = 20$ nm Cu film (spectra of MIN samples with other nanohole arrays in Supporting Information). In brief, this is because the resonance is reasonably strong and in the red region of the visible for Cu nanohole arrays of these dimensions. Even though the resonances should be sharper for $h = 30$ nm films (indicated in Fig. 1D), thicker films are not preferable since the reflectivity increases in the spectral regions outside the resonantly reflected color, which reduces the chromaticity. Concerning Al_2O_3 thickness, the best RGB primaries were achieved with approximately 75 nm for red, 103 nm for blue and 115 nm for green. (Note that these values are highly sensitive to the refractive index of the film, which may vary slightly with deposition technique etc.) The corresponding reflectivity spectra in air were measured at an incident angle interval from zero up to 41° (Fig. 2B) using an air objective with NA 0.8. Importantly, despite this wide range of viewing angles the reflectivity is around 90% for each metasurface in the red, green or blue region respectively. The chromaticity (Fig. 2C) of the three primary colored metasurfaces was analyzed as described previously,¹¹ showing that the gamut has the D65 white point included and covers 27% of the standard RGB. This so called CIE 1931 xy diagram is the established way of illustrating the chromaticity. Each color within the triangle is accessible by linear combinations (subpixels) of the coordinates of the primaries.

A photo of large-area metasurfaces representing the primaries is shown in Fig. 2D, illustrating the intense colors. (This photo, like other photos below, is taken with an ordinary mobile phone camera under normal lighting conditions with standard settings and the image has not been manipulated.) The red color was not improved by introducing nanoholes in the top film due to the

surface plasmons excited in this spectral region, as confirmed by the reduced reflectivity when nanoholes are present in Cu (dashed spectrum in Fig. 2B), in agreement with previous results for Au nanohole arrays.³² Note that the reflectivity is reduced despite the wide angular interval in the measurement because the scattering occurs mainly at even higher angles (to the surface normal) for nanohole arrays of these dimensions.¹¹ Therefore we did not use nanoholes for the red metasurfaces (and strictly speaking they are not plasmonic), but we emphasize again that the plasmonic nanoholes are necessary for achieving green and blue metasurfaces (as well as cyan and yellow), which are otherwise more magenta colored due to the increased reflectivity in the red. Numerical simulations of the reflectivity from MIN structures with literature values for permittivity^{28, 30} further confirmed the role of the surface plasmons (Supporting Information).

After optimizing the primary colors, we reproduced digital photos with the MIN metasurfaces by three standard photolithography steps (one each for patterning red, green and blue). Fig. 3A shows a “white standard” sample generated by RGB stripes, each 30 μm in width. Upon switching to dark field illumination we could verify that the blue and green metasurfaces scatter yellow and red light respectively, confirming the plasmonic activity from the nanoholes in Cu. As a control, there is no scattering detected from the red stripes since this is not possible for a thin film system without lateral structures. Color images were produced by translating each pixel in the source file into a RGB triplet with the relative intensities varied through the length of each subpixel stripe. Fig. 3B shows an example of such pixels 30 μm wide and from zero to 100 μm long. Several photos were successfully reproduced by the metasurface RGB pixels. (Some results cannot be shown here due to copyright issues.) In Fig. 3C we present a photo enabling a direct comparison between the pixelated plasmonic MIN structures and printing using a laserjet printer on ordinary paper. In both cases, the same image is reproduced, which is a colorful photo of the “Kuggen”

building on our University campus in Gothenburg (source image included as Supporting Information). The metasurfaces clearly reproduce images very well in terms of colors. Importantly, this is despite the fact that for any other color than full white, only a fraction of the area contains metasurfaces. Still, the image clarity is obviously comparable to printed dyes on paper because of the high reflection. The image quality is further improved by the fact that both the cavity mode and the surface plasmon excitation are only weakly dependent on polarization³³ and viewing angle (Supporting Information). The resolution is higher for the plasmonic image (282 dpi) and can be further improved since the limit is set by the optical lithography.

Figure 3. Reproducing color images by RGB pixel triplets. (A) RGB stripes 30 μm in width generate a white sample. In dark-field illumination, scattering of the complementary colors is observed for green and blue metasurfaces, while the red structure without nanoholes gives no scattering. (B) Microscopy example image of metasurfaces patterned into RGB triplet with varying subpixel areas. (C) Photo providing a comparison between laserjet printing and plasmonic metasurfaces. The image reproduced shows the “Kuggen” building at the University campus.

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The most important step towards active plasmonic displays operating in reflection mode, i.e. electronic paper, is to implement electric modulation of the reflected intensity. Besides liquid crystals, this can be achieved with conductive (π -conjugated) polymers that switch between light absorbing and transparent states, such as polypyrrole.³⁴ Continuous Au structures or Au nanoparticles on a transparent conductor such as indium tin oxide (ITO) can remain stable while acting as one electrode to facilitate electrochromic switching of a conducting film on top of the metal. However, other metals like Cu are typically very unstable in electrolytes.²⁶ Although the top Al_2O_3 layer of the MIN structures was sufficient to provide excellent stability in air for our metasurfaces, they were quickly destroyed when potentials were applied in an electrolyte. In order to make the structures compatible with electrochemistry we first deposited an additional insulating SiO_2 coating of approximately 100 nm. Next, to enable electrochromic switching, we used the highly conducting electrochromic polymer poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT is known to provide sufficient conductivity (also in its low-conductivity state) to facilitate its own switching without a supporting electrode.^{34, 35} It also provides a high and quite homogenous electrochromic contrast throughout the whole visible wavelength range, i.e. it essentially switches from black to transparent, albeit with a blue tone in the dark state.^{35, 36} Thin films of PEDOT doped with polystyrene sulfonate (PEDOT:PSS) were screen-printed onto the metasurfaces, demonstrating compatibility with large-scale manufacturing.³⁶

Electrochromic devices were finalized by immersing the polymer-modified metasurfaces in simple electrolytes and using ITO covered (25 nm) plastic as opposite window and counter electrode (Fig. 4A). The reflectivity changes upon switching the PEDOT (± 1 V) in phosphate

buffered saline (PBS) are shown in Fig. 4B (dashed vs full lines) for each primary colored metasurface. The reflectivity difference is >0.4 in the red region (for the red metasurface) and somewhat lower (~ 0.3) for blue and green metasurfaces. By using plastic supports we could make electrochromic devices that were flexible and the radius of bending was limited simply by the thickness of the plastic support relative to the device area. Fig. 4C shows examples of devices and the color changes upon switching the voltage. Note that the PEDOT was always prepared directly on the MIN structures (separated only by the thin SiO_2 film). This is important because if the “shutter” is at a large distance from the colored surface proper image display in pixel arrays is problematic. This is a well-known limitation with LCD displays where the relatively thick liquid crystal layer⁴ required for good contrast restricts the viewing angle. In our active devices the absolute reflectivity in the “on” state (full lines in Fig. 4B) is reduced compared to the bare metasurfaces in air (Fig. 2B). This is in part because the PEDOT:PSS layer is not entirely transparent in the bright state, but also due to the electrochemical cell in the reflection spectroscopy setup. We emphasize that these results prove that electrochromism can be implemented on the nanostructures and although the optical contrast is sufficient for simple reflective displays³⁶ there is clearly room for further optimization, for instance with respect to polymer thickness and composition³⁵ (discussion in Supporting Information). The thickness of the screen printed PEDOT:PSS films in this work was approximately 500 nm as measured by a profilometer (not shown).

Figure 4. Electrochromic switching. (A) Cell design. (B) Reflectivity spectra of PEDOT-modified metasurface in the on and off states. (C) Pictures of a flexible device and electrochromic switching of the metasurfaces (approximately 2×2 cm² shown). (D) Switching dynamics (at 536 nm) for a blue metasurface. The voltage is reversed between +1 V and -1 V as indicated by the arrows.

Example of switching dynamics for a metasurface coated with PEDOT:PSS are shown in Fig. 4D (5 cycles). More than 90% of the reflectivity change occurs in less than 1 s, which represents

a response time suitable for electronic readers and simpler segmented reflective displays. The current trace gave a switching energy of 5.7 mJ/cm^2 (Supporting Information). Assuming an update every $\sim 10 \text{ s}$ as typical for electronic readers, the power density for a display based on this technology is well in the ultralow region and even lower than electrophoretic ink.³⁷ Further, PEDOT has good bistability or “optical memory”,³⁴ i.e. the power consumption for maintaining an oxidation state (the same image in a reflective display) is extremely low. We refer to a video available as Supporting Information showing fast switching and bistability in a red device. The lifetime of the devices in terms of switching cycles can be very high since PEDOT can undergo hundreds of cycles depending on the environment.³⁵ However, any defects in the SiO_2 protection layer leading to contact between the nanostructure and the electrolyte would gradually destroy the samples.

In conclusion, we have shown that MIN metasurfaces combining Cu and Al can provide high chromaticity and intense reflection almost independent of polarization. Using RGB subpixels with varying area this enabled reproduction of color images of high quality over large areas using only abundant metals. Furthermore, the metasurfaces were made electrochromic by insulating the MIN structure with SiO_2 followed by printing of PEDOT:PSS, which can be used for new types of reflective displays. The most challenging next step is to implement transistor arrays with the electrochromic switching³⁶ in order to fully realize “plasmonic electronic paper” based on only abundant metals. The polymer composition and thickness can be further optimized for each primary color. There are also technical details that can be addressed to improve device stability and performance, such as increasing the charge capacity of the transparent counter electrode.³⁸ Plasmonic electronic paper could fill a gap among existing display technologies by providing flexible reflective displays in color, thereby overcoming the limitations of electrophoretic ink (no

colors) and reflective LCDs (low reflectivity and not bendable). At the same time other advantages are maintained, such as excellent visibility in direct sunlight, extremely low power consumption and even health benefits compared to emissive displays.³⁹

ASSOCIATED CONTENT

Supporting Information

Experimental details. Reflectivity of metasurfaces with other Cu nanohole arrays. Simulated reflectivity of metasurfaces. Calculated dispersion relations. Data of current during PEDOT switching. Angle and polarization dependence. Photo of metasurfaces with only Al. Discussion on optimal polymer layer. The following files are available free of charge:

Image of the “Kuggen” building (Kuggen.tif)

Video showing switching and bistability of a red electrochromic device (bistability.avi)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MIN, metal insulator nanohole array; ITO, indium tin oxide; PEDOT poly(3,4-ethylenedioxythiophene); RGB, red-green-blue; LCD, liquid crystal display; PBS, phosphate buffered saline.

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