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Bioinspired microstructured polymer surfaces with antireflective properties

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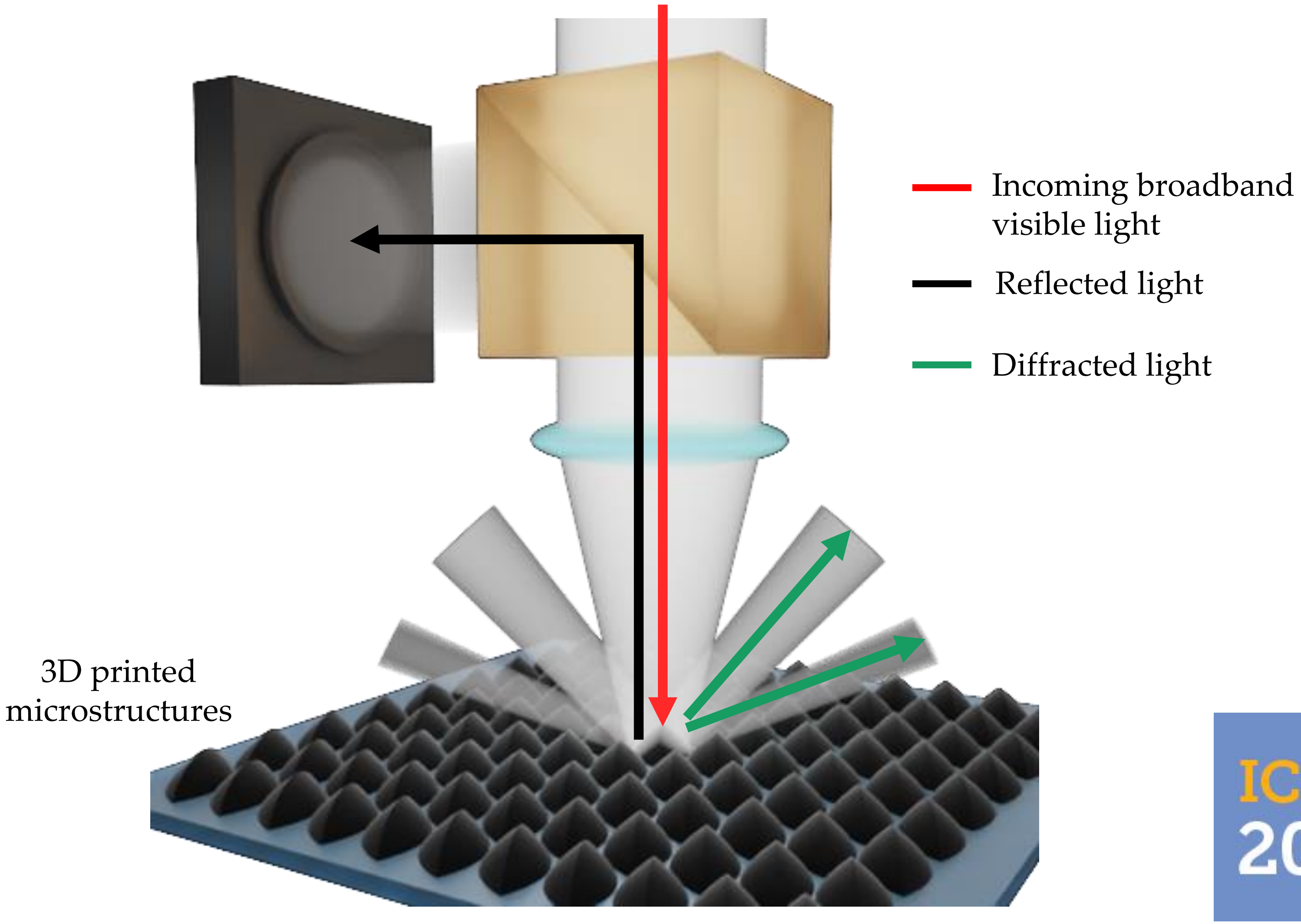

Bioinspired microstructured polymer surfaces with antireflective properties

Abstract:

Over the years, different approaches to obtaining antireflective (AR) coatings have been explored such as using index-matching, interferences or micro- and nanostructures. In 2002, a novel super black surface was developed by Brown *et al.* at the National Physical Laboratory in UK, and soon gained significant interest among both academia and industry. Since then, scientists have been competing in a race to produce the blackest material.

Structural colors are ubiquitous in nature and therefore an interesting way to develop AR coatings is biomimicry. Moth-eye structures are well-known and have been successfully replicated using micro- and nanofabrication. However, other animal species such as birds of paradise and peacock spiders also display super black features.

In this presentation, we present the fabrication and characterization of AR microarrays inspired by the peacock spiders' super black structures encountered in nature. First, a 3D model of the structures is generated using a surface equation. Second, fabrication is done by super-resolution 3D printing using two-photon polymerization. Third, the resulting structures are imaged by scanning electron microscope (SEM). Finally, we characterize the structures reflectance and transmittance at normal incidence using a dedicated optical setup.

Keywords: Antireflective coating; Biomimicry; Super black; 3D printing

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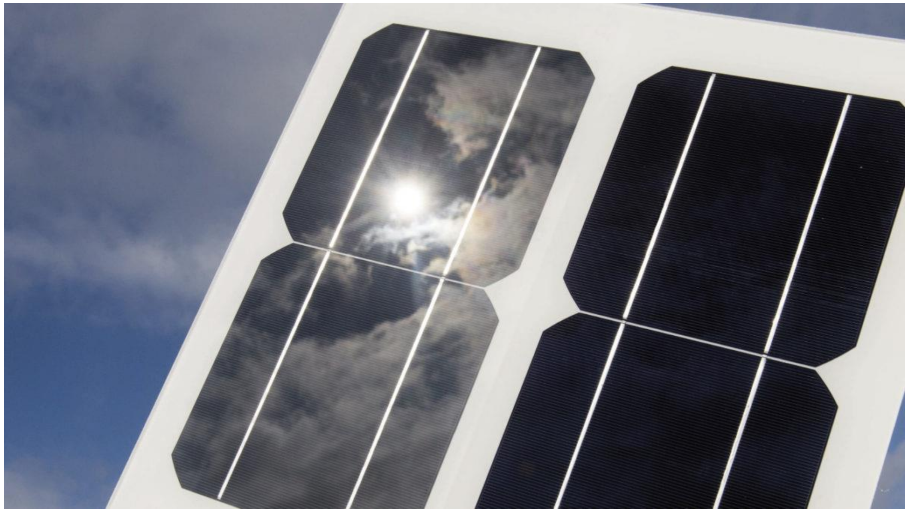
Introduction AR coatings and applications

Antireflective (AR) structures or coatings can be used for a large palette of applications. A few common examples are:

1. **Imaging optics:**
   Minimizing losses from reflections on components such as lenses, mirrors, etc.
2. **Optical communication:**
   Minimizing losses over large distances in optical fibers.
3. **Solar cells:**
   Maximizing solar cells efficiency by avoiding light reemission/enhancing absorption.
4. **Photolithography:**
   Optimizing printing of small or high aspect ratio features, e.g. by using bottom antireflective coating (BARC)

[1] https://newvisionopticallab.com/anti-reflective-coating/



[2] https://www.pv-magazine.com/2019/01/26/the-weekend-read-reflections-on-a-soiled-module/

Introduction AR coatings and applications

AR can be obtained using different mechanisms:

Interference (thin films):

By playing with the film thickness and the refractive index (RI) for a single layer (SL) thin film on a substrate, we can create destructive interferences between the incoming wave and the wave reflected from the substrate for a given wavelength. Using multi-layer (ML) coatings, antireflection over a larger wavelength range and incident angles range can be achieved. Fig. 1 illustrates both the SL and ML thin films' reflectance.

[3] https://www.microglobe.co.uk/info/multi-coated/index.html

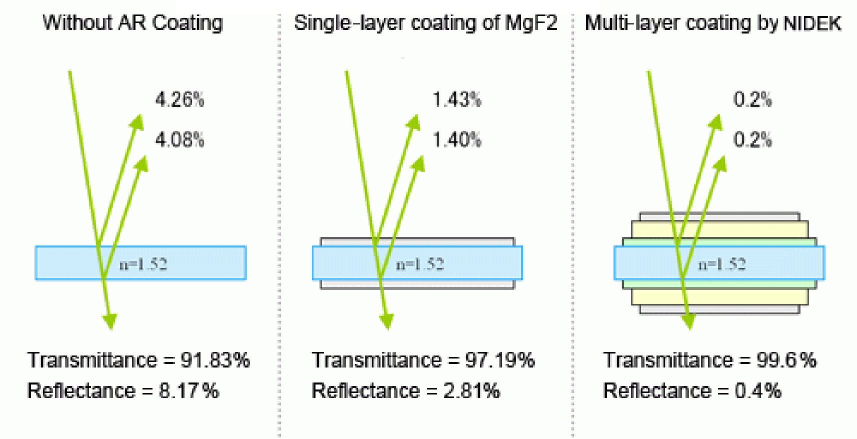


Fig. 1: Example on the effect of SL (middle) and ML (right) AR coating as compared to no coating (left)[3]

Gradient refractive index:

Since the reflectance is principally due the change in refractive index (e.g. from air to substrate), one way of obtaining broadband low reflective materials is by creating a gradient refractive index profile between the two materials of interest. Different gradient index profiles can be created, such as the ones showed in Fig. 2.

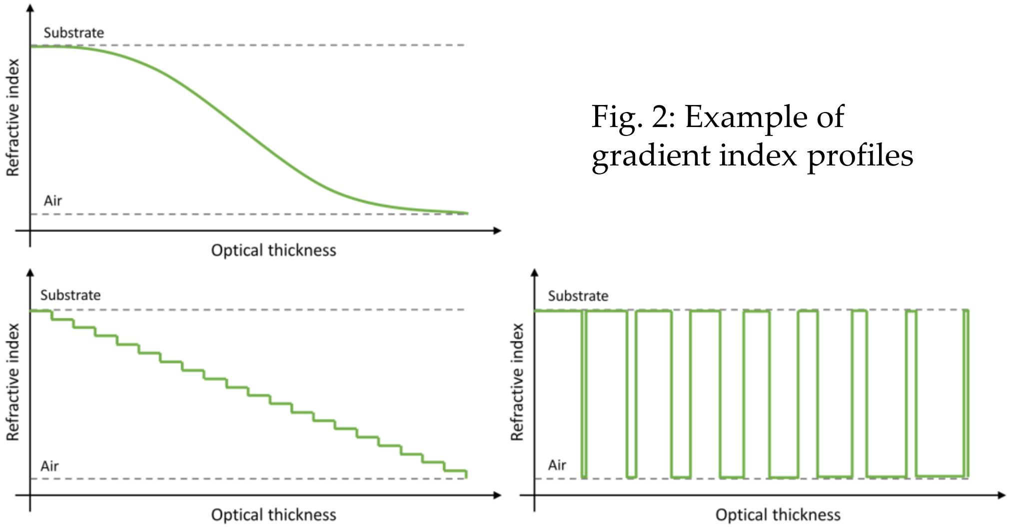


Fig. 2: Example of gradient index profiles

Introduction AR coatings and applications

AR can be obtained using different mechanisms (continued):

Macroscopic rough surfaces:

Creating a macroscopic rough surface can enhance the AR properties of a material by its effect on the surface scattering properties. This includes for example multiple internal reflections and diffraction from periodic structures (Fig 3.a)

Sub-wavelength rough surfaces:

When the wavelength is larger than the surface pattern, the surface acts as a gradient index film and reduces reflection (Fig. 3.b)

[5] Cai, J. & Qi, L. Recent advances in antireflective surfaces based on nanostructure arrays. *Mater. Horizons* **2**, 37–53 (2015).

Hierarchical structures:

Both effects can be further combined into structures with both a macro and a micro pattern (Fig. 4).

[6] Okulova, N., Johansen, P., Christensen, L. & Taboryski, R. Effect of structure hierarchy for superhydrophobic polymer surfaces studied by droplet evaporation. *Nanomaterials* **8**, (2018).

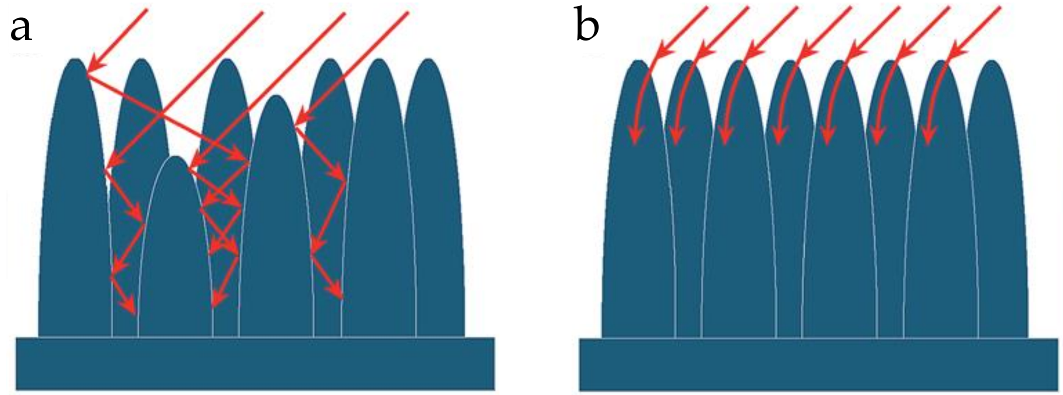


Fig 3: Macroscopic and microscopic rough surface effect on reflectance.[5]

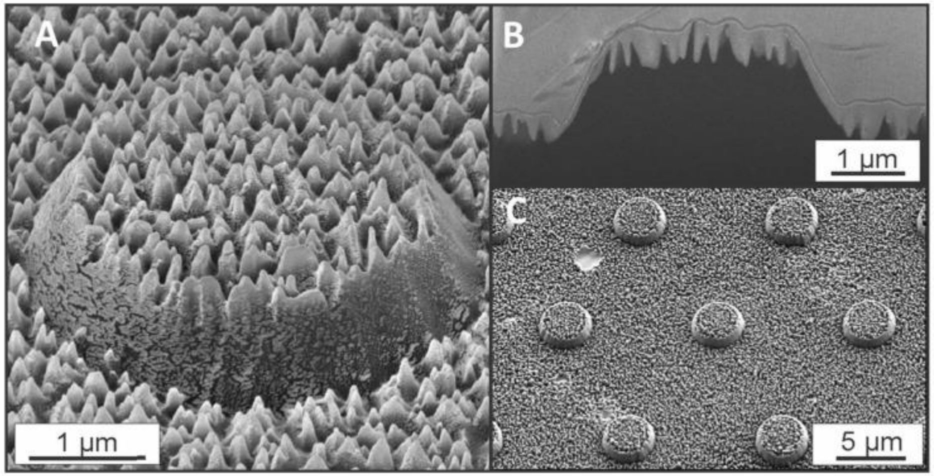


Fig 4: Example of hierarchical structures.[6]

Introduction Super black materials

Recently, some materials such as Vantablack from Surrey NanoSystems[7] have attracted a lot of attention because of their very low reflectance. These are commonly referred to as "super black" materials in reference to the nickel-phosphorous alloys first developed by the National Physical Laboratory (NPL), Teddington, Middlesex, UK.[8] These alloys were first shown to have a reflectance around 0.35% across the visible spectrum. Nowadays, Vantablack is manufactured by growing a forest of carbon nanotubes on a surface and achieves a reflectance lower than 0.2% on average over the visible spectrum (400-750 nm).

Although the term "super black" is commonly used to refer to a material or surface exhibiting very low reflectance, no exact definition of this term can be found in literature.

In our case, we consider the following definition of super black inspired from McCoy et al.[9]:

> A material/structure/surface is considered to be super black if it displays less than 0.5% reflectance for a given wavelength range.

Fig. 5: Vantablack material covering a portrait sculpture as demonstrated by Surrey NanoSystems [7]

[7] https://www.surreynanosystems.com/assets/media/vantablack-vb-a4-data-brochure-2016.pdf

[8] https://www.eurekalert.org/pub_releases/2003-05/npl-hbi052803.php

[9] McCoy, D. E. *et al.* Structurally assisted super black in colourful peacock spiders. *Proc. R. Soc. B Biol. Sci.* **286**, (2019).

Introduction

Biomimicry

Fig. 6: Moth eyes with repeating micropattern[10] composite rough structures.

Fig. 7: Male bird of paradise with super black feathers enhancing the blue color from other feathers.[11]

Another way of creating super black materials is by getting inspiration from nature. Most noticeably, moth eyes, feathers from birds of paradise and fur patches on peacock spiders have all been found to display super black properties (see Fig. 6-8).

While studies have tried replicating the moth eyes' structures, no one – to the best of our knowledge - has reported the creation of structures inspired from the birds of paradise or peacock spider's fur.

In this study, we therefore show the replication of the peacock spider's microlens structures using two photon polymerization (2PP) 3D printing.

Fig. 8: Male peacock spider with bright colors enhanced by super black structures.[12]

[10] https://physicsworld.com/a/moth-eyes-inspire-more-efficient-solar-cell/

[11] https://www.livescience.com/61406-black-hole-bird-of-paradise.html

[12] https://www.sciencemag.org/news/2019/05/superblack-patches-these-spiders-make-their-other-colors-glow

Microstructure design

Peacock spiders display bright colors enhanced by super black regions. These low reflectance regions are created by a combination of both microlenses-like structure and an absorbing layer[9].

We designed our structures using the methods from McCoy et al.[9] where the structures are defined using the following surface equation:

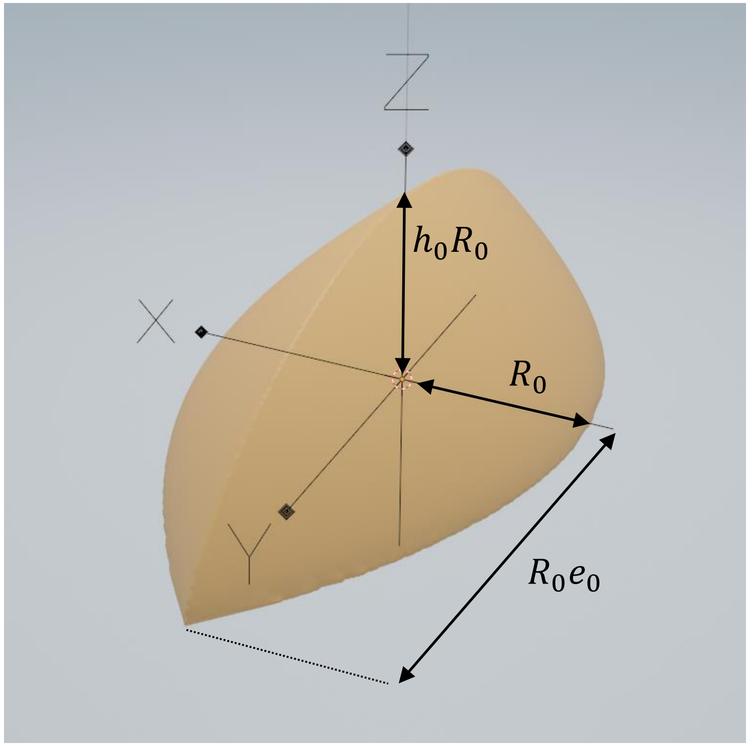


Fig. 9: Example of microlens structures generated with parameters $R_0 = 5$ arb. unit, $h_0 = 2$, $e_0 = 2$ and $N = 1$

$$z(x,y) = R_0 h_0 \left(1 - \left|\frac{x}{R_0}\right|^N - \left|\frac{y}{R_0 e_0}\right|^2\right)^{-\sqrt[2]{2N}}$$

Where R_0 is the structure size, h_0 is the height, e_0 the elongation and N the shape parameter (N=2 gives an ellipsoid, whereas N=1 is close to a pyramid).

The structures files were created in the Matlab software and then converted to a format adapted for 3D printing. An example of such structure can be seen in Fig.9.

[9] McCoy, D. E. *et al.* Structurally assisted super black in colourful peacock spiders. *Proc. R. Soc. B Biol. Sci.* **286**, (2019).

Results 2-photon polymerization printing (2PP)

The structures found on peacock spiders have typically a structure size of 2.5-5 µm (R_0).

In order to fabricate such structures with a large accuracy, we used a two-photon polymerization 3D printer. 2PP makes use of very localized, short pulse laser beams to trigger two photon absorption in a given resin.

While 2PP is suited for rapid prototyping, it also permits to reach a very good lateral resolution of around 200 nm for the features created.

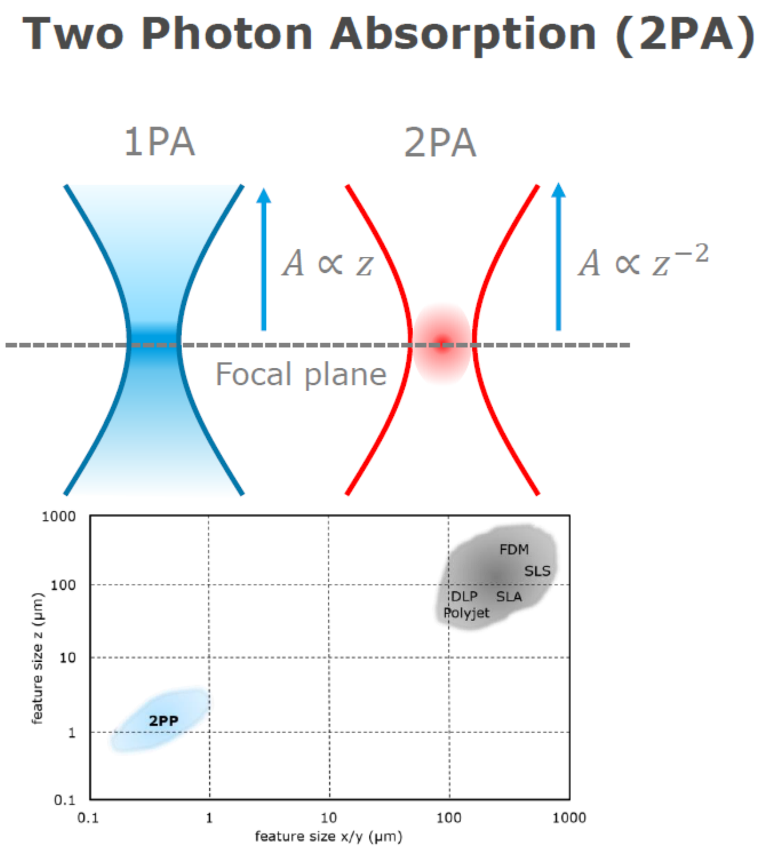


Fig. 10: Principle of two-photon absorption for two-photon printing (2PP)[13].

[13] © 2007-2021 Nanoscribe GmbH & Co. KG

Results

SEM images of printed structures

The structures were printed on glass coverslips and were packed as closely as permitted by the design. For a shape parameter of $N = 2$ and an elongation $e = 1$, the printed structures correspond to hemispheres and are packed in an hexagonal array. For other shape parameters and elongation, the array lattice parameters were adapted to leave as little space as possible on the substrate.

Examples of the printed structures can be seen in Fig. 11.

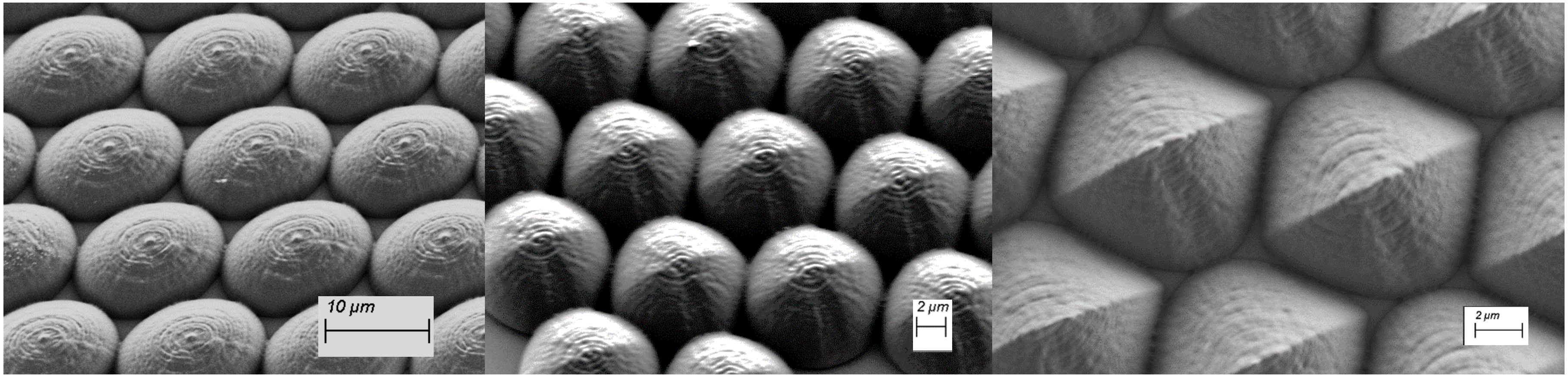


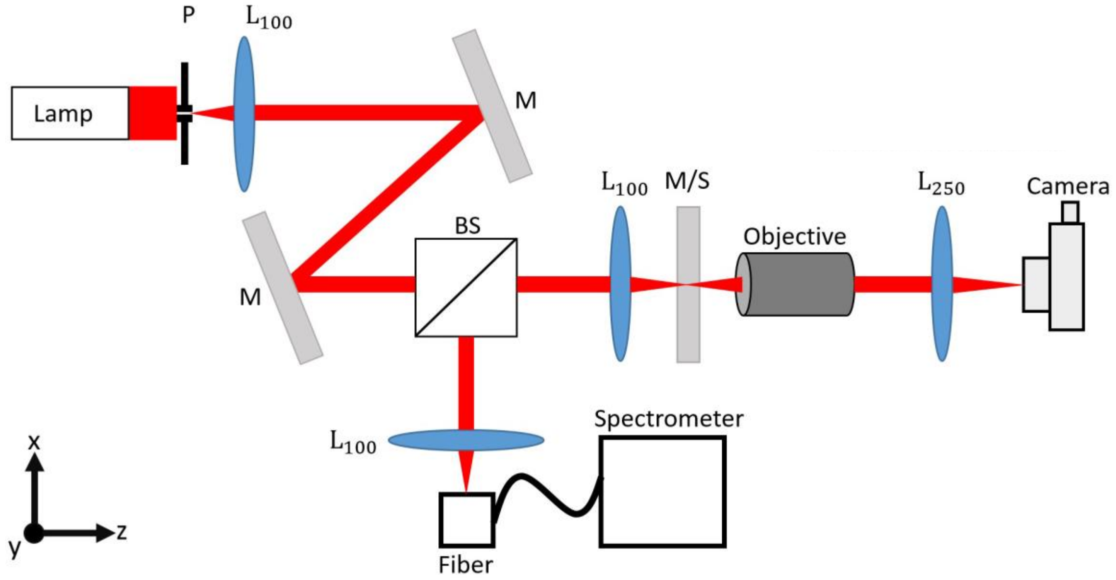
Fig. 11: SEM images of structures printed using 2PP. Left: hemispheres. Middle: structures with e = 1 and $N = 1.5$. Right: structures with e = 1 and $N = 1$.

Results

Optical reflectance setup

We measured both the transmittance and reflectance from the printed structures using the optical setup shown in Fig. 12.

Fig. 12: Schematics of the optical reflectance measurement setup used.



A halogen lamp is used as the light source and illuminated a pinhole (P, Ø = 100 μm). The pinhole is imaged onto the printed microlenses using two relay lenses. The reflected light is then collected at normal incidence using one additional lens and a beam splitter (BS), before being transmitted to a spectrometer. The sample (S) is first replaced by a broadband mirror (M) in order to get a reference spectrum. The reflectance was then calculated as the ratio between the sample measurement and the reference measurement.

In addition, we imaged the transmitted light from the samples into a camera using an microscope objective and a lens. In the same way as for the reflectance, a measurement without any sample is used as a reference and the transmittance is calculated as the ratio between the samples measurement image and the reference image.

Results & Discussion

Optical reflectance measurements (1)

As a first step for our investigation, we printed hemispheres with radius (R_0) from 2 to 10 µm. The average reflectance spectrum over at least 3 different samples can be observed in Fig. 13, and the computed average values over the visible spectrum (400 to 700 nm) can be seen in Table 1.

Apart from two peaks around 400 and 750 nm respectively, the reflectance spectra are relatively flat in the visible range, with reflectance values reaching below 0.5%.

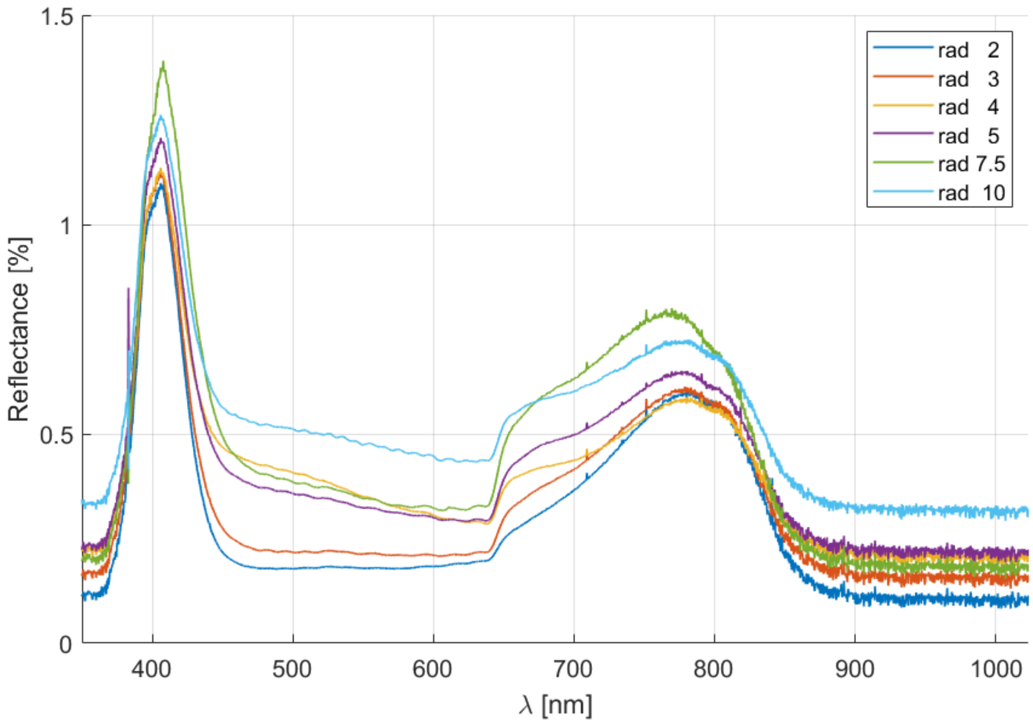


Fig. 13: Reflectance spectra of the printed hemisphere arrays for different radii (R_0) in µm.

On average over the visible spectrum, the structure reflectance can be defined as super black as it reaches below 0.5% except for the largest structure sizes here of 10 µm. We can also see a decrease in reflectance with a decrease in structure size, although radius 4 and 5 µm give very similar results.

Radius [µm]	Average Reflectance ± std [%]
2	0.279 ± 0.013
3	0.320 ± 0.012
4	0.436 ± 0.014
5	0.432 ± 0.013
7.5	0.495 ± 0.016
10	0.565 ± 0.013

Tab. 1: Average reflectance values for the visible range (400 to 700 nm).

Optical reflectance measurements (2)

We plot now the reflectance data from Fig. 13 at a wavelength of 550.02 nm (see Fig. 14.a). We can again see a lower reflectance here for the smallest structures and a larger reflectance for the biggest structures. For structure size in between, the reflectance shows similar values.

In addition, we used a camera to retrieve the transmittance for the same structures (see Fig. 14.b). Even though we obtain here values that correspond to an average over the camera pixels spectral response, it gives a good overview of whether the light is transmitted the structures rather than scattered. We can see here that the transmittance is between 60 and 70% for structures of radii 4 to 10 µm and lower for smaller structures.

The smaller transmittance and reflectance for smaller structures can be explained by larger diffractions angles from the repeating patterns. For smaller pitch, the diffracted light will be sent at larger angles and will not be collected by our setup lenses.

To minimize reflectance while maximizing transmittance, structures with a radius of 4 or 5 µm look therefore like good candidates.

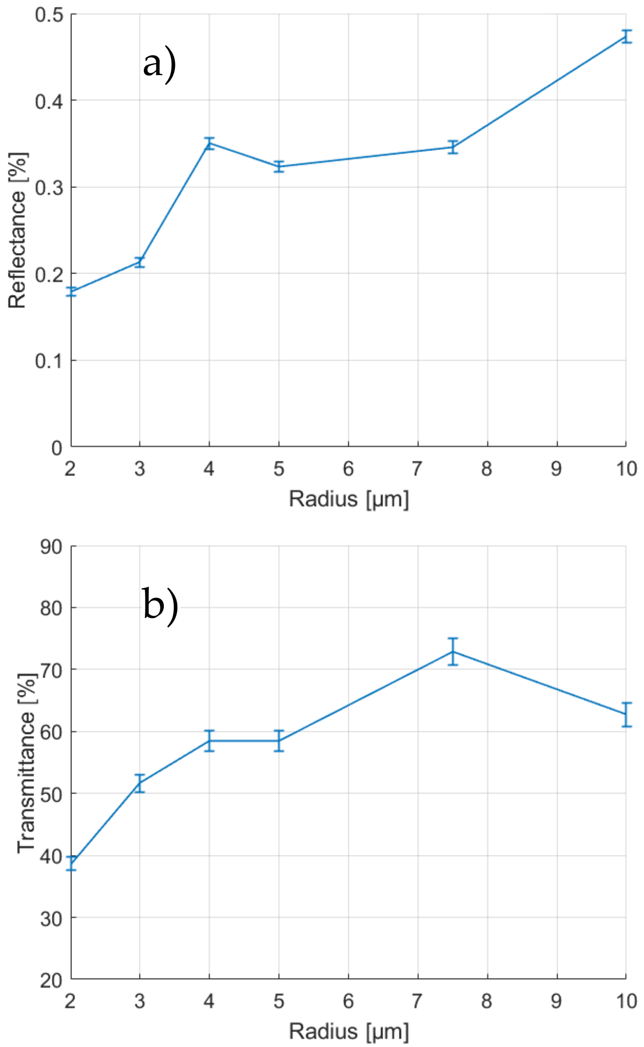


Fig. 14: a) Reflectance at $\lambda = 550.02$ nm, b) Transmittance measured from the camera

Conclusions

In this presentation, we have shown that:

- Biomimicry is a powerful tool when it comes to designing structures for AR applications.
- Nanostructures are not the only way to achieve super black AR properties.
- 2PP 3D printing is an efficient method to create super black structures inspired from the peacock spiders' fur.

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