

Nanopages

Optical properties of bioinspired disordered photonic nanoarchitectures

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Optical properties of bioinspired disordered photonic nanoarchitectures

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Abstract

Bioinspired 1+2D nanoarchitectures inspired by the quasi-ordered structures occurring in photonic nanoarchitectures of biological origin, like for example butterfly scales, were produced by depositing a layer of SiO₂ nanospheres (156 nm and 292 nm in diameter) on Si wafers, over which a regular multilayer composed from three alternating layers of SiO₂ and TiO₂ was deposited by physical vapor deposition. Flat multilayers were deposited in the same run on oxidized Si (324 nm SiO₂ thickness) for comparison. Different types of disorder (in plane and out of plane) were purposefully allowed in the 1+2D nanoarchitectures. The positions of the specular reflection maxima for the flat multilayer and for the two different bioinspired nanoarchitectures were found to be similar. Additionally to this, the bioinspired nanoarchitectures exhibited angle independent diffuse reflection too, which was absent in the flat multilayer. Different model calculations were made to explain the specular and diffuse optical properties of the samples. Satisfactory agreement was obtained between experimental data and model calculations.

Keywords: bioinspired; structural color; disordered; nanospheres; diffuse reflection; light coupling

1. Introduction

Photonic crystals are a particular case of nanocomposites. Taking the concept of photonic crystals in a strict sense,¹ due to the rigorously periodic alternation of the refractive index

1 from high to low values in a three dimensional (3D) structure, and provided that the high/low
2 contrast has a high enough value, in certain wavelength regions, called the stop-gaps, the
3 nanocomposite will not allow the propagation of the electromagnetic waves (EMW).¹ Later
4 on, the concept was significantly extended to include metallic photonic nanoarchitectures² and
5 partially³⁻⁵ or fully disordered systems too.^{6,7} Nowadays, photonic crystals are regarded as
6 particular case of the broader category of metamaterials.⁸ There is a growing interest to the
7 field of photonic crystals that comes from the ability of the photonic crystals to manipulate
8 and control light propagation in three dimensions in space. On the other hand, the
9 manufacturing of defect free large area 3D photonic crystals is still a technological challenge.⁹

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22 Interestingly enough, biological evolution, also "discovered" the photonic nanoarchitectures
23 as a very versatile way of producing color.^{10,11} Most frequently, the photonic
24 nanoarchitectures of biologic origin are characterized by a certain degree of disorder, which
25 may affect their optical properties significantly.¹² It was shown recently for nine closely
26 related butterfly species that the structural color is generated by well-defined characteristic,
27 quasi-ordered structures, with a well-defined species specific color, which is used as a sexual
28 recognition signal.¹³ Due to this, the very same color originating from quasi-ordered photonic
29 nanoarchitectures is reproduced with a great degree of fidelity generation by generation.

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43 The knowledge, extracted from the investigation of biological, partially or fully disordered
44 photonic nanoarchitectures, could provide photonic structures with structurally more robust
45 and with more versatile optical properties than artificial opals for example. In the same time,
46 the manufacturing of such nanocomposites could be a lot less demanding than the production
47 of fully ordered 3D nanoarchitectures. There is a growing interest to artificially made quasi-
48 ordered structures,¹⁴ similar to the ones found in nature and gone through several million
49 years of evolution. This may lead to new manufacturing procedures and may help in the
50 discovery of new bioinspired structures. The purpose is not to copy the structures exactly
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which is difficult technologically and could be very expensive, rather to learn and understand the principles of biological structures and use them to fabricate photonic structures with novel properties. We used this approach in this paper.

In the present paper we made photonic nanoarchitectures in which a certain degree of disorder has been introduced purposefully. Similar nanoarchitectures have been prepared earlier, but the role of disorder and how the disordered structures may interact with light were given less consideration.^{15,16} We investigated the optical and structural properties in detail, and we propose several models to understand in which ways the basic geometry and the disorder of the nanoarchitectures interact with light.

2. Materials and methods

The photonic nanoarchitectures modeling the butterfly scales with a certain degree of disorder were produced in several steps. First, the silica particles were prepared according to Stöber's method using tetraethyl orthosilicate (TEOS), absolute ethanol and ammonium hydroxide.¹⁷ Different amounts of ammonium hydroxide were used to prepare silica particles of two different diameters (156 nm, 292 nm). 3 inch silicon wafers covered with native oxide were used as substrates for the deposition of the nanoparticles. For the single layer deposition, a Langmuir-Blodgett trough was used.¹⁸ As it was not our aim to produce fully ordered layers, no special care was taken to precisely compact the dispersed nanospheres on water surface before the substrate was vertically ejected from water. Fully ordered or fully disordered samples can be produced under well-defined conditions, while the conditions under which partially ordered, or quasi-ordered samples can be produced - like those occurring in butterfly wings^{11,12} - are less well defined.

In a subsequent step the nanoparticles were anchored to the surface by the conformal growth of a 5 nm thick alumina layer by atomic layer deposition (ALD) method.^{19,20} The ALD

1 process was carried out using a Picosun Sunale R-series ALD reactor at 300°C with
2 trimethylaluminium precursor and water. This anchoring process was necessary because in
3
4 the previous experiments when thin films were deposited by Physical Vapor Deposition
5 (PVD) onto the monolayer of nanospheres, the growing film caused the degradation of the
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7 nanosphere film continuity and the exfoliation of the layer. After ALD, the samples were
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9 characterized by atomic force microscopy (AFM).
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15 In the next step 3 pairs of alternating TiO₂/SiO₂ layers, each with 65 nm thickness, were
16 evaporated onto the sample by PVD. TiO₂ and SiO₂ were used as high and low refractive
17 index materials, respectively, without significant absorption coefficient in the visible
18 spectrum, to minimize the absorption within the multilayer. In parallel with the nanosphere
19 layers, bare microscope slides and silicon wafers covered with native oxide and with 324 nm
20 thermal oxide were also subjected to PVD to be used as reference samples.
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31 After the full deposition cycle was completed the samples were characterized again by AFM
32 and SEM. Optical characterization of the flat multilayers was done by spectral ellipsometry
33 and in a spectrogoniometric setup using an Avantes 2048 fiber-optic spectrometer.³ In the
34 spectrogoniometric setup, the samples were illuminated perpendicular (0°) to the sample
35 surface, and the reflectance was measured from 10° to 80° with 5° resolution. Ellipsometric
36 measurements were done on a multilayer coated glass and silicon wafer substrates without
37 nanospheres to precisely determine the thicknesses and refractive indexes of the deposited
38 layers. The measurements were performed by a Woollam M-2000DI rotating compensator
39 ellipsometer in the spectral range of 190-1700 nm. It showed that the thicknesses of the
40 layers, counted from the substrate were very close to the preset value (65 nm): 64.7 nm, 61.7
41 nm, 67.7 nm, 62.3 nm, 66.6 nm, 67.1 nm.
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58 **3. Computational details**

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1 As the above described photonic nanoarchitectures are composed from nanostructures with
2 1D and 2D periodicity, their properties could be discussed separately with different models.
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4 The optical properties of a 1D multilayer can be modeled by transfer matrix method. In our
5 model we used an ideal plane parallel multilayer (without interface roughness and with
6 invariant thicknesses). This simple multilayer model contains 9 layers on top of a silicon
7 substrate, counted from the substrate: native oxide, 156 or 292 nm SiO₂ depending on the
8 diameter of the spheres, 5 nm Al₂O₃ and 3 pairs alternating TiO₂ and SiO₂ layers. In our
9 models, we used the thicknesses that were measured experimentally by ellipsometry on the
10 flat reference samples.
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22 The effect of the 2D periodicity can be modeled by 3D numerical calculations and was
23 performed using the MEEP implementation of the finite-difference time-domain (FDTD)
24 method.²¹ Our model systems were built up using the experimentally measured data, the cross
25 section of the geometry can be seen in Fig 1. The native oxide layer and the alumina layer
26 were neglected, since the thickness of these layers is much less, or comparable with the spatial
27 resolution, and we tried to use the simplest model in order to separate the different effects. At
28 two parallel sides of the simulation box that are perpendicular to the sample surface, Bloch
29 periodic boundary conditions were set to make possible the reduction of the size of the
30 computational cell (perpendicular to the cross section that can be seen on Fig. 1.). On the
31 other sides, perfectly matched layer (PML) absorbing boundary conditions were set. The
32 structure was excited by a Gaussian planewave source with a wide wavelength domain (200 -
33 1000 nm). The electric field of the source was polarized in two reciprocally perpendicular
34 directions in a plane, parallel to the sample surface to take into account the unpolarized light
35 source used in the experiments. For calculating the specular reflection flux (F_{refl}), the detector
36 plane was placed parallel and slightly below the source plane. The intensity of the incoupled
37 light was calculated on the detection plane placed into the multilayer (F_{layer}). In order to get
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1 the reference incident flux, we performed a simulation without the model photonic
2 nanoarchitecture and measured the flux below the source plane (F_{refl} plane on Fig. 1. without
3 the geometry).
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7 **4. Experimental results**

8 *4.1 Structural investigation*

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11 Atomic Force Microscope (AFM) measurements were done on the silica nanosphere
12 monolayers, deposited by Langmuir-Blodgett method and stabilized by ALD deposited
13 alumina layer. The two layers showed quite different morphology (Fig. 2.).
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22 The layer built of smaller spheres had monolayer domains with crystalline order. It also had
23 an out-plane disorder: many creased islands could be found in the layer, forming a second
24 layer on the top of the first layer. The creased islands were found to be only a few 100 nm
25 distances from each other. The average sphere distance (156 ± 7 nm) was calculated from
26 several line cuts not running through the creased islands, assuming closed packing.
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35 The layer built of larger spheres showed only a short range order. This type of in-plane
36 disorder or quasi-ordered structure can be found in the scales of butterflies and can be
37 characterized by Fast Fourier Transformation (FFT).^{12,22} A similar method can be used in this
38 case to determine the average distance of the spheres and to characterize the disorder of the
39 layer. With this method the diameter of the spheres cannot be determined exactly, since the
40 FFT power spectrum contains only the structural information parallel to the surface, in other
41 words the distance of the neighboring spheres. The FFT power spectrum calculated from the
42 AFM image, showed a ring-like feature around the origin (Fig. 2f.). This means that the
43 spheres are arranged randomly but have a characteristic distance from each other. On the
44 radial average of the power spectrum (Fig. 2e.) a clear peak can be seen according to the ring
45 on the FFT image. The position of the peak can be calculated by fitting a Gaussian, the
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1 average distance of the spheres was 292 ± 12 nm. The real sphere diameter may be somewhat
2 smaller, because it is hard to measure precisely the average diameter of the spheres with AFM
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4 when the spheres are not arranged in a closed packing, so the diameter was satisfactorily
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6 approximated with the distance of the neighboring spheres. The disorder of the samples can
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8 also be seen after the $\text{TiO}_2/\text{SiO}_2$ multilayer deposition on Fig. 3.
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11 12 13 *4.2 Specular reflectance*

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16 Multilayers should have only mirror-like (specular) reflection. Since these samples are
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18 basically multilayers with two dimensional quasi-periodic roughness, it is worth to investigate
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20 the specular reflection and compare it to conventional plane multilayers.
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24 Comparing the experimental data of the simple multilayer reference and the nanoarchitectures
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26 (Fig. 4.), when illuminated and measured perpendicular to the sample surface, one may
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28 remark a clear difference in the intensities of the reflectance maxima. The measured
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30 reflectance values on the nanostructured samples were about half of the corresponding values
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32 of the flat multilayer reference sample (Fig. 4.). This finding is not surprising if the roughness
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34 of the samples, caused by the sphere layers, is taken into account. One of the main effects
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36 expected from the irregularities in the sample structure is the appearance of scattered light.
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38 Furthermore, the size of the nanospheres did not have a marked influence on the intensity of
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40 the reflection peaks, this means that the same mechanism was responsible for the reflection of
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42 the two samples with nanospheres.
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48 49 *4.3 Diffuse reflectance*

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52 Diffuse (Lambertian) reflection cannot be observed on conventional multilayers, since these
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54 structures have only mirror-like reflection. While on the layered structures discussed in this
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56 paper, a noticeable diffuse reflection was found. When illuminated under perpendicular
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58 incidence to the surface with white light, as compared with the specular samples, both
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1 nanoarchitectures built with the smaller and the larger nanospheres reflect light with higher
2 intensity into all directions in the wavelength range of 400-500 nm (Fig. 5.). This is reason of
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4 the clearly seen blue color of the nanoarchitectures opposite to the black of the regular
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6 multilayer. This similar behavior should be caused by similarities in the structure of the
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8 samples. The only similarity in the samples is the $\text{TiO}_2/\text{SiO}_2$ multilayer, evaporated onto the
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10 sphere layers. Therefore it could be presumed that the nanospheres and the undulated
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12 multilayer are responsible for the diffuse reflected wavelength range.
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18 If comparing the two nanoarchitectures with each other, one may remark a much stronger
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20 angle dependence of the reflected light intensity in the case of the smaller spheres, while the
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22 sample with the larger spheres exhibits a plateau in the range of 30° to 60° .
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26 One may remark from Fig. 5. c-f. that the corrugated sample with the smaller nanospheres
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28 exhibits a stronger color dependence of the reflected diffuse light with the angle of
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30 observation as compared with the sample with larger nanospheres. The later ones appear blue
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32 over the entire angular range; this corresponds to the plateau seen in Fig. 5b. The naked eye
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34 observation and the spectrogoniometric data are fully in agreement. This is a clear proof that
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36 such structures are suitable to produce an angle independent structural color in a similar way
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38 like the scales of Lyceanid butterflies.¹³
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43 **5. Discussion**

44 *5.1. Specular reflection*

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47 To be able to explain the specular reflection, the different properties of the samples have to be
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49 separated. We have seen that the specular reflection of reference sample and the samples with
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51 nanospheres have been similarly composed of several peaks. We suppose that this similarity
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53 is caused by the multilayer structure of every sample. This could be investigated by simple 1D
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55 calculation, where the 2D structure of the samples parallel to sample surface is not taken into
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1 account. The 1D model gave a very close specular reflection to the measured ones; the only
2 discrepancy is the intensity difference (Fig. 6.). Therefore we can conclude that mainly the 1D
3 multilayer structure is responsible for the position of the reflection peaks.
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7 The 2D structure of the samples could be taken into account with a more complex 3D model.
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9 In these calculations we used perfectly ordered 3D FDTD structures with closed packed
10 triangular lattice, this allows us to separate the effect of the disorder in the samples. Although
11 the 3D FDTD model uses only constant refractive indexes, it gives better coincidence
12 between the computed and the measured spectra. The refractive indices were chosen at the
13 wavelength of 530 nm, because our model not allowed to use wavelength dependent
14 refractive indices. The refraction index of the SiO₂ and TiO₂ varies more for smaller
15 wavelengths, what means that the constant refractive index approximation gave larger
16 discrepancy. A more refined model could be used by building the whole reflectance spectrum
17 from several calculations which use different values of refractive indexes for different spectral
18 ranges (Table 1.). In this model, we used the refractive indexes of the materials at the
19 wavelength of the measured reflectance maxima, and this model also gave better fit to the
20 experimental results in the smaller wavelength range.
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40 The 1D models used for the two different samples predicted about twice as high reflectance
41 maxima than the measured ones in the wavelength range of 500 - 600 nm. On the other hand
42 the FDTD calculations predicted the correct intensities. This means that the roughness and the
43 3D structure of the samples caused the experimentally found lower intensities, as compared to
44 the flat multilayers.
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51 In the FDTD model calculations we used a perfectly ordered 3D FDTD structure. As no
52 characteristic differences can be found between the specular reflectance measurements and
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1 the calculations, we can conclude that the disorder of the samples has only a minor effect on
2 the specular reflection.
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4 5 *5.2. Diffuse reflection* 6

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9 3D FDTD calculations in contrast with the 1D calculation are capable of better explaining
10 how light interacts with the structure. The calculations showed that a large part of the
11 incoming light penetrated to the multilayer, and propagated parallel to the sample surface,
12 even a small out scattering of this propagating mode could be seen (Fig. 7.). This propagating
13 mode could be a good explanation of the diffuse reflection properties.
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22 Unfortunately, direct comparison between the measurements and the calculations cannot be
23 made, since the light intensity within the multilayer cannot be measured or the intensity of the
24 scattered light in the far field cannot be calculated in the currently used model. In order to
25 compare quantitatively the measured light scattered under non-specular angles with the
26 calculations, the following procedure was used: the sample was illuminated under normal
27 incidence (0°), and light scattered under different angles was collected using the
28 spectrogoniometric setup. To use a simple 2D presentation of the essentially 3D experimental
29 data and to be able to compare in a simple way the two samples with nanoarchitectures, all
30 acquired spectra were averaged over the detecting angle. For each individual curve used in the
31 averaging the same white diffuse standard was used as a comparison sample.
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47 In the calculations, the spectrum of the incoupled light was measured within the multilayer
48 (Fig. 1., on an F_{layer} plane close to the source), then the intensity was doubled to take into
49 account the light that propagates to the opposite direction ($F_{\text{calculated}}$ on Fig. 8.). In these
50 models the refractive index of the materials were set to the values corresponding to 430 nm,
51 where the measured diffuse peaks with the highest amplitude are found. For the larger
52 nanospheres, the calculations showed a similar reflection peak as the measurements and give
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1 a very good agreement with the measured curves (Fig. 8.). It can be also seen that a large
2 amount (approx. 70%) of the incoming light incouple into the multilayer.
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5 This good agreement also means that the in-plane disorder does not affect the reflection
6 properties of the samples too much, because perfectly ordered closed packed ordering were
7 used in our calculations in contrast to the disorder of the measured samples. On the other hand
8 the clearer understanding of how this in-plane disorder affects the reflection needs more
9 extended models (supercells) where the quasi-ordered structure can be modeled in more
10 detail. For the smaller spheres, our FDTD model cannot reproduce the reflectance spectrum.
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12 We will discuss this in detail later.
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23 In the calculations, we have seen that a large amount of the incoming light incoupled to the
24 multilayer with a spectrum very close to the measured ones. We could then conclude that the
25 diffuse reflection could be modeled by the out scattering of this propagating mode, as it can
26 be seen on Fig. 7. We have made another calculation with a longer cell, where the fluxes were
27 measured in the multilayer on several positions (F_{layer} on Fig. 1. with different horizontal
28 positions). It showed that the intensity of the reflection peak decreased with the distance from
29 the source, what can be explained by the out scattering of light (Fig. 9.).
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41 *5.3. Role of the structural disorder in the optical properties*

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44 On the model sample with the smaller spheres, we have seen that the calculated spectrum did
45 not match with the experimental diffuse reflection. We assume that the multilayer structure
46 has a nearly flat surface and light cannot incouple into it. As the size of the nanospheres is far
47 from the wavelength of the illuminating light the in-plane nanostructure of the layers has less
48 effect. It was shown by the AFM and SEM measurements that in the experiments there are
49 creased islands where the evaporated multilayer are rougher. These surface irregularities may
50 cause that light can more easily be incoupled into propagating modes in the structure.
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To test this hypothesis, different 3D geometries were used in model calculations. Four geometries were created; each of them had one sphere under the radiation source plane which was raised slightly above the sphere layer. The cross sections of the geometries can be seen in Fig. 10. The blue area represents the region below the radiation source plane. By these small modifications, a 5 to 10 times intensity increase in the wavelength range of 350-550 nm can be achieved and correlated with the measured diffuse reflectance. The calculations also showed that the effectiveness of this coupling also depends on the vertical and horizontal position of the raised sphere. On the other hand, several calculations need to be done with different possible geometries of the creased island to achieve better fit to the measurements.

It is worth to observe that the two different kinds of disorder yield different behavior. The calculations on an ordered model with the larger spheres adequately reproduced the measured reflection curves. This shows that the in-plane disorder of the samples had less influence on the diffuse reflection spectra. On the other hand, the influence of the out of plane disorder on an in-plane ordered structure to the diffuse reflection, in the case of samples with smaller spheres, was satisfactorily reproduced by raising a sphere from the monolayer in the FDTD calculations.

6. Conclusions

We have created two kinds of 1+2D layered nanoarchitectures without perfect crystalline order using a 1D multilayer on top of 2D nanosphere layers. Such structures can be regarded as simplified models of nanostructures occurring in natural photonic nanoarchitectures, like butterfly wing scales. The two nanosphere layers had quite different structure. The sample with smaller nanospheres had a more ordered in-plane structure, but was exhibiting creased islands (out of plane disorder). The sample with larger nanospheres had a stronger in-plane

1 disordered structure exhibiting only short range order. The disorder was characterized by
2 Fourier Transformation.
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5 Detailed spectroscopic measurements revealed that the 1+2D nanoarchitectures behave as
6 intermediates between a simple 1D multilayer and a Lambertian reflector. They exhibited
7 similar reflectance maxima in specular geometry as a regular, flat multilayer, but also
8 exhibited a nonspecular component in the reflected light under any other angle of observation.
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10 This nonspecular, diffuse component is similar to the behavior of photonic nanoarchitectures
11 with disordered nanostructures found in nature.²³ Several models were done to understand and
12 interpret the optical properties of the samples.
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23 Simple multilayer model showed that the reflection peaks in the specular reflectance spectra
24 of the nanoarchitectures came from the multilayered structure of the samples. On the other
25 hand, more complex 3D FDTD models showed that the decreased intensity of the reflection
26 peaks came from the roughness of the multilayer, caused by the sphere layer. The in-plane
27 disorder of the samples however seemed that did not have marked influence to the specular
28 reflection.
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39 The 1 + 2D nanoarchitectures exhibited diffuse reflection in the entire spectral range. Both
40 structures had a characteristic simple peak or a double peak around the 430 nm. Detailed 3D
41 calculations showed that after light was incoupled into the nanoarchitecture, it propagated in
42 the undulated multilayer in a direction parallel to the sample surface. The experimentally
43 measured peaks come from the out-scattering of this light coupled into a propagating mode in
44 the multilayer, because of the roughness of the multilayer and probably due to the defects.
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1 Simulations showed that a large amount of the incoming light with this characteristic
2 wavelength continues to propagate in the multilayer. It was also shown that a small out of
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4 plane modifications in the smaller sphere layer - as the creased islands were modeled - can
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6 drastically increase the intensity of the light incoupled into propagating modes. In the 3D
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8 models we used a perfectly ordered lattice of the spheres. However, the experimental samples
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10 showed that the layer of larger spheres had only short range order, the measured specular and
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12 diffuse reflection of the sample could be well interpreted by the calculations and no
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14 characteristic effect was found on the reflection of this type of disorder.
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20 Experimental data and computer modeling proved, that using well known multilayers that can
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22 easily be constructed with well established material science methods, more complex
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24 structures can be made which can be seen from a wide viewing area. The disorder (in-plane,
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26 out-plane), the properties of the multilayer (layer thicknesses and refractive indexes) provide
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28 several possibilities of further experiments to fine-tune the optical properties.
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33 **Acknowledgments**

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36 The work in Hungary was supported by OTKA grant PD83483.
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Figure and table captions

Figure 1. Cross sectional geometry of the 3D FDTD model. The position of the source plane and the detector planes (F_{layer} and F_{refl}) were also shown. The position of the F_{layer} was varied in the different calculations to investigate the propagating mode in the multilayer. The materials that are used: gray – silicon substrate; blue – SiO_2 ; green – TiO_2

Figure 2. AFM (a, b, d) images of the layers of silica nanospheres with two diameters: (a-b): 156 nm, (d): 292 nm. (c) Fast Fourier transformed AFM image on the sample with smaller spheres, three of the ordered lattice directions are labeled by arrows. (e) The calculated radial average of the power spectrum on the sample with larger spheres. (f) Fourier transformed AFM image on the sample with larger spheres, the lack of long range order can be seen.

Figure 3. SEM images of the samples after $\text{TiO}_2/\text{SiO}_2$ multilayer deposition with (a) smaller spheres, (b) larger spheres and (c) a multilayer reference with 324 nm thermal oxide layer on silicon substrate. The cross section of the structures and the roughness of the surface of the samples can be seen.

Figure 4. Specular reflection of the samples with spheres, and a flat sample with thermal oxide layer below the multilayer. The illumination and detection were perpendicular to the sample surface.

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Figure 5. Diffuse reflection of the samples: a) smaller, 156 nm spheres and b) larger, 292 nm spheres with multilayer on top. The illumination was perpendicular to the sample surface. High reflection can be seen under every detection angles around the wavelength range of 400-500 nm on both figures, but the angle dependence on the sample with larger spheres is much smaller. c – f) Photo of the samples with the same illumination setup (perpendicular to the sample surface). The samples from left to right: nanoarchitectures with 156 nm spheres, nanoarchitectures with 292 nm spheres, multilayer reference sample with 324 nm oxide. The angle of observation is c) 10°; d) 30°; e) 45°; f) 60°. Note that in agreement with the data in (a) the nanoarchitecture with 156 nm spheres changes color with the increasing of the viewing angle, while the color of the nanoarchitecture with the 292 nm spheres - in agreement with (b) - is essentially constant under all viewing angles. The flat multilayer does not exhibit any color when viewed under oblique angles.

Figure 6. Calculated specular reflection of the samples with 1D model, and 3D FDTD models. Samples with a) smaller spheres and b) larger spheres.

Figure 7. Time evolution ($t_1 < t_2 < t_3$) of the electric field perpendicular to the cross section (E_y) and the horizontal Pointing vector (S_x) with a wavelength around 435 nm, where the diffuse peak was found. The nanoarchitecture was built of the larger 292 nm spheres. The propagating mode in the S_x images and the out scattering of light in the E_y images can be seen. The blue colours are negative; the red ones are positive values.

Figure 8. Average diffuse reflectance of the samples with respect to a white diffuse standard (R_{measured}), compared to the calculated values by FDTD model ($F_{\text{calculated}}$).

Figure 9. Intensity of the propagating light within the multilayer in the samples with larger spheres. The distances, given in the upper right corner, were measured from the plane in the

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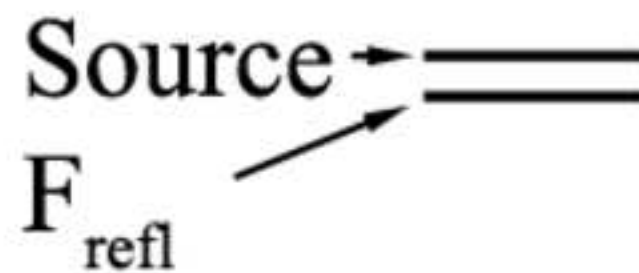
multilayer below the center of the source. The reflection maximum decreased to 50 % at about 2500 nm distance from the source.

Figure 10. 3D FDTD calculations were done on smaller spheres (156 nm diameter) with modified geometries, where a sphere was raised above the sphere layer. The cross-section of the geometries can be seen on the right side, the blue area represents the regions below the radiation source plane. By the small modification, a significant increase by 5 to 10 times can be observed in the wavelength range of 350-550 nm.

Table 1. Refractive indexes and spectral ranges that were used in the refined 3D FDTD model

Figure1
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Source →
 F_{refl} ↗

A diagram showing a source of waves on the right, represented by two parallel horizontal lines. An arrow labeled "Source" points to the right towards these lines. A second arrow labeled F_{refl} points from the lines back to the left, representing a reflected wave.

F_{layer}

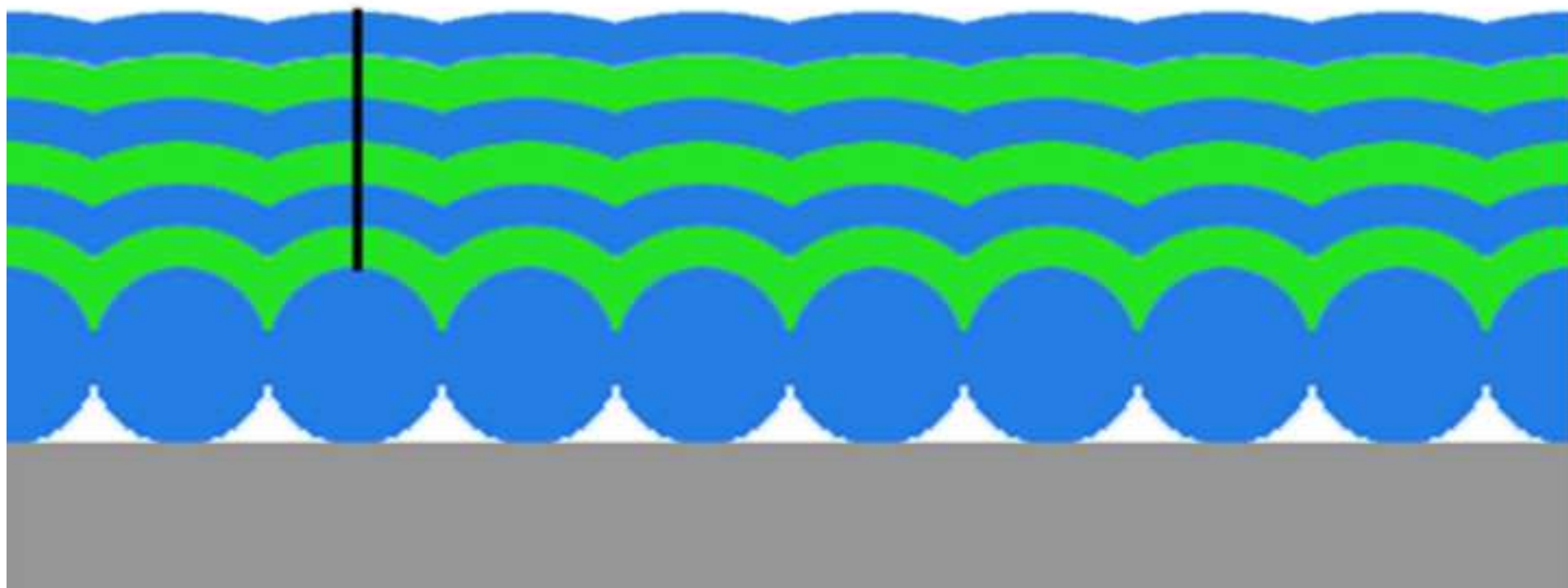
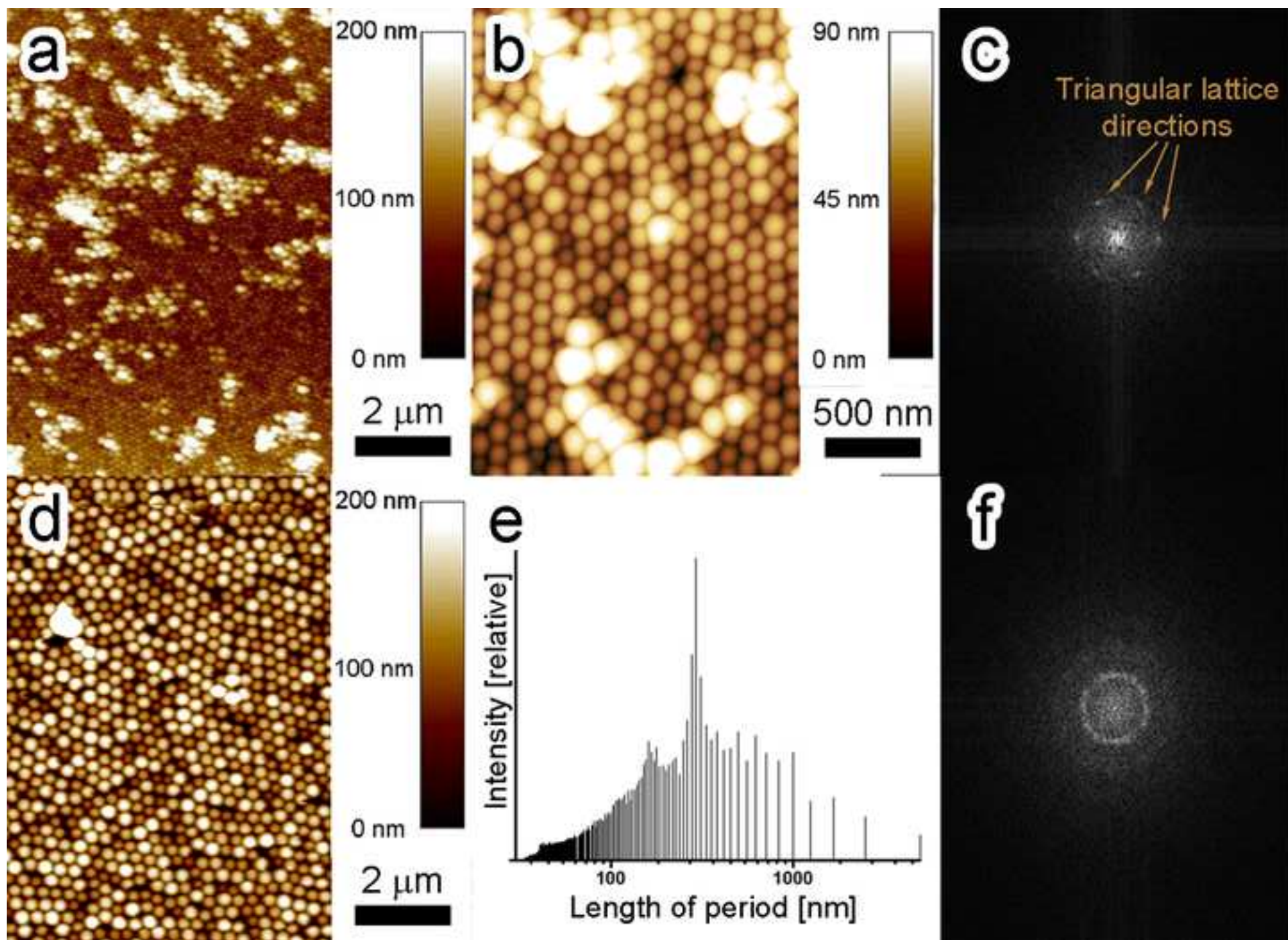


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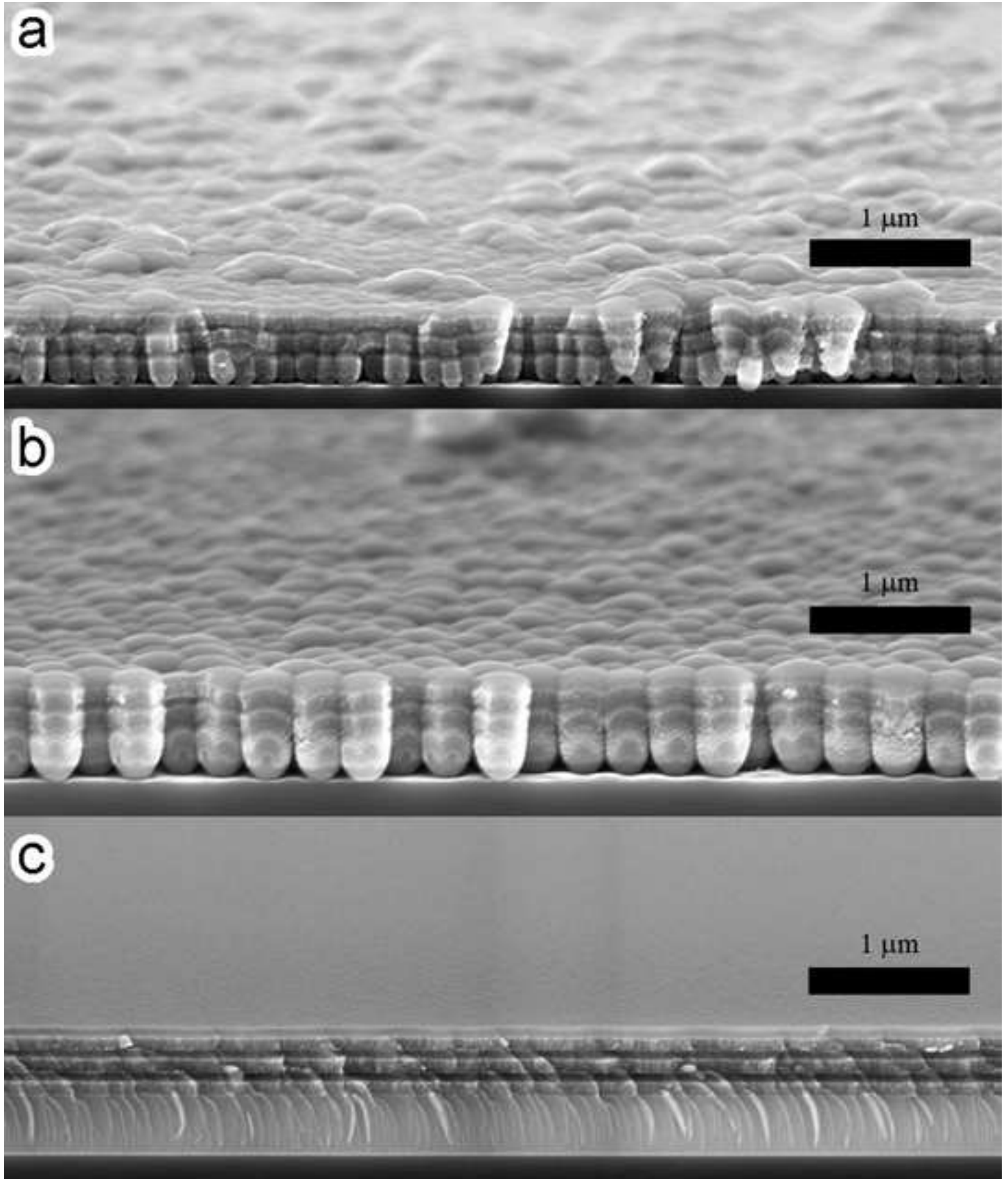


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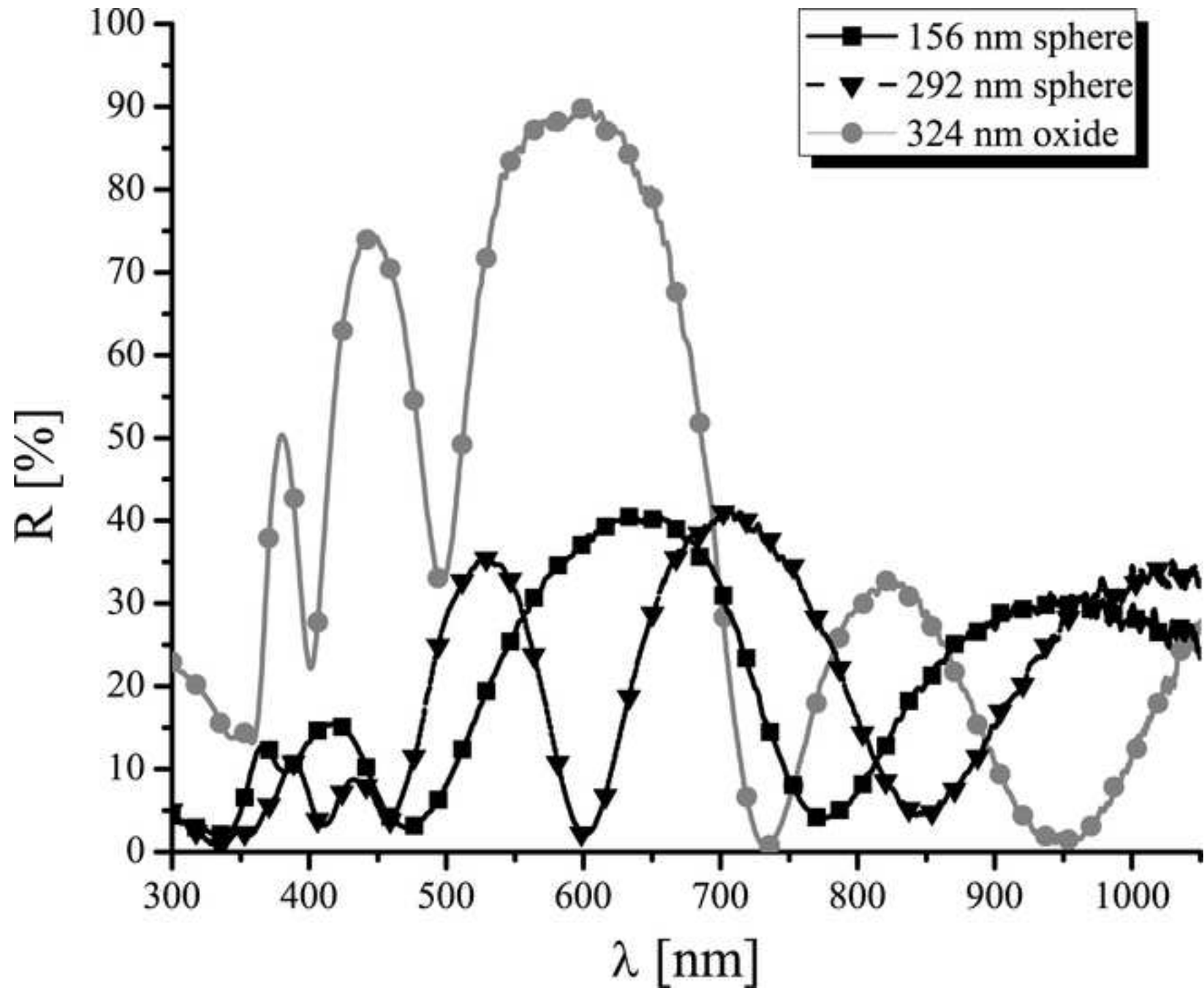


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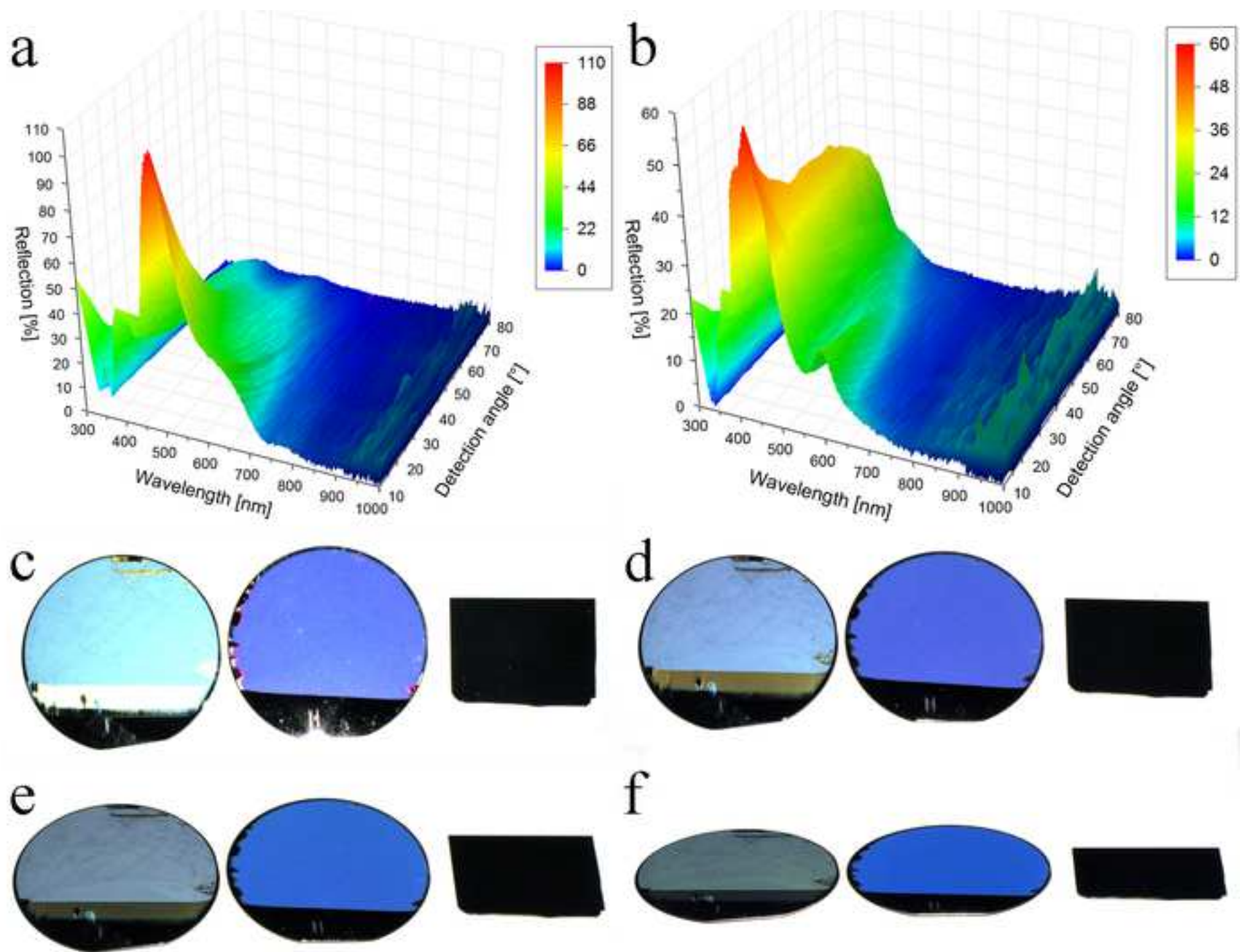


Figure6
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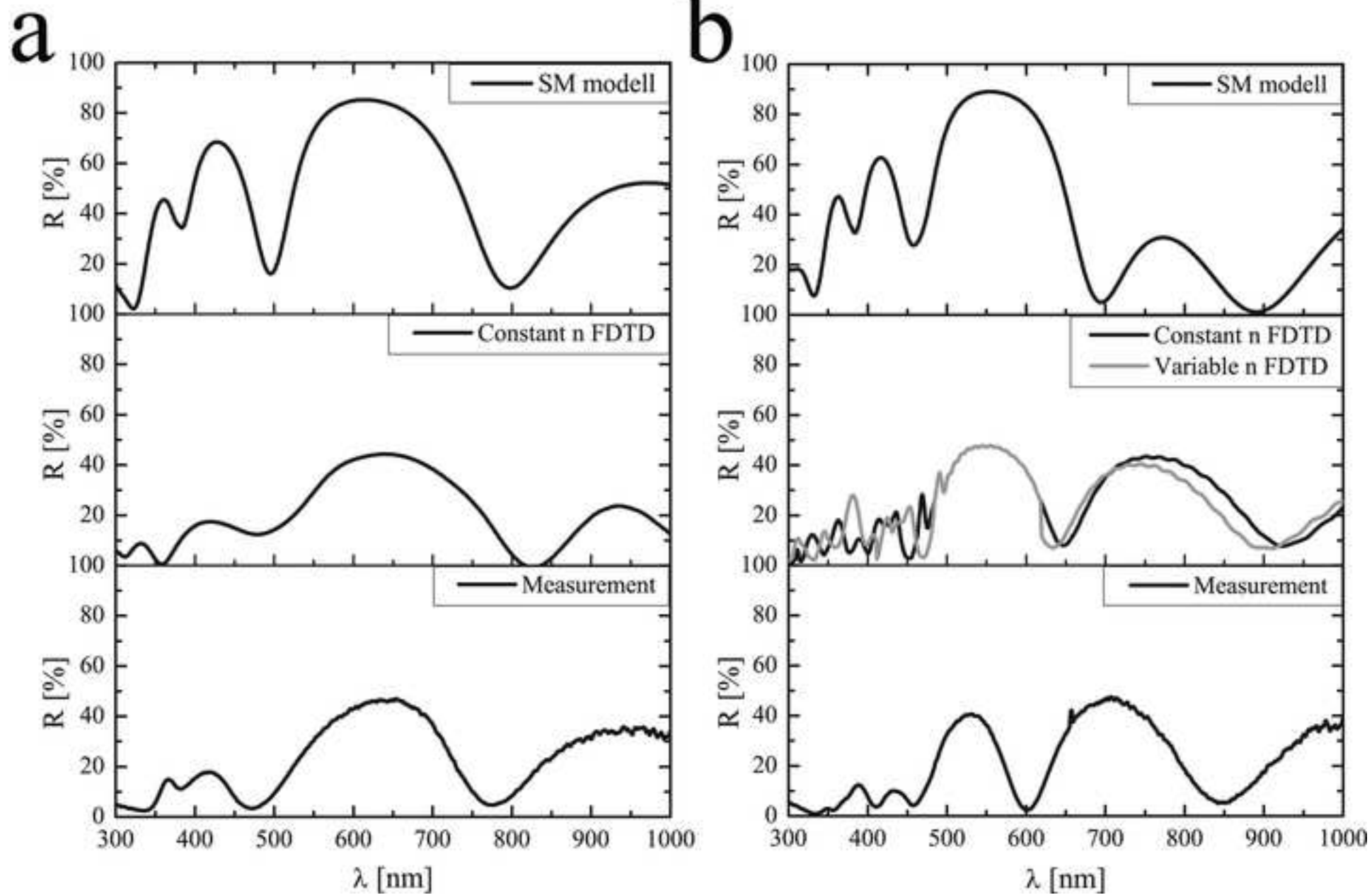


Figure 7
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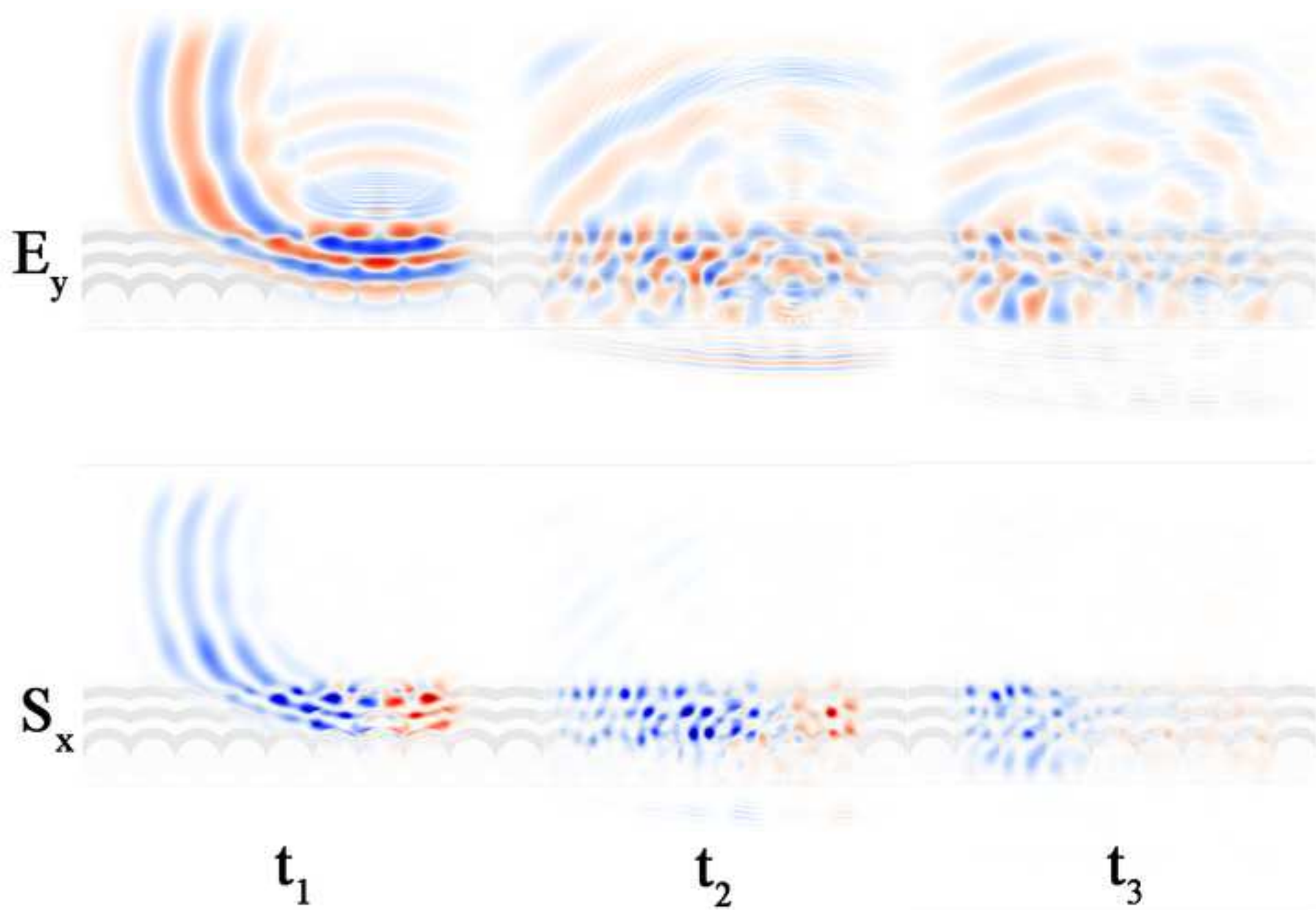


Figure8
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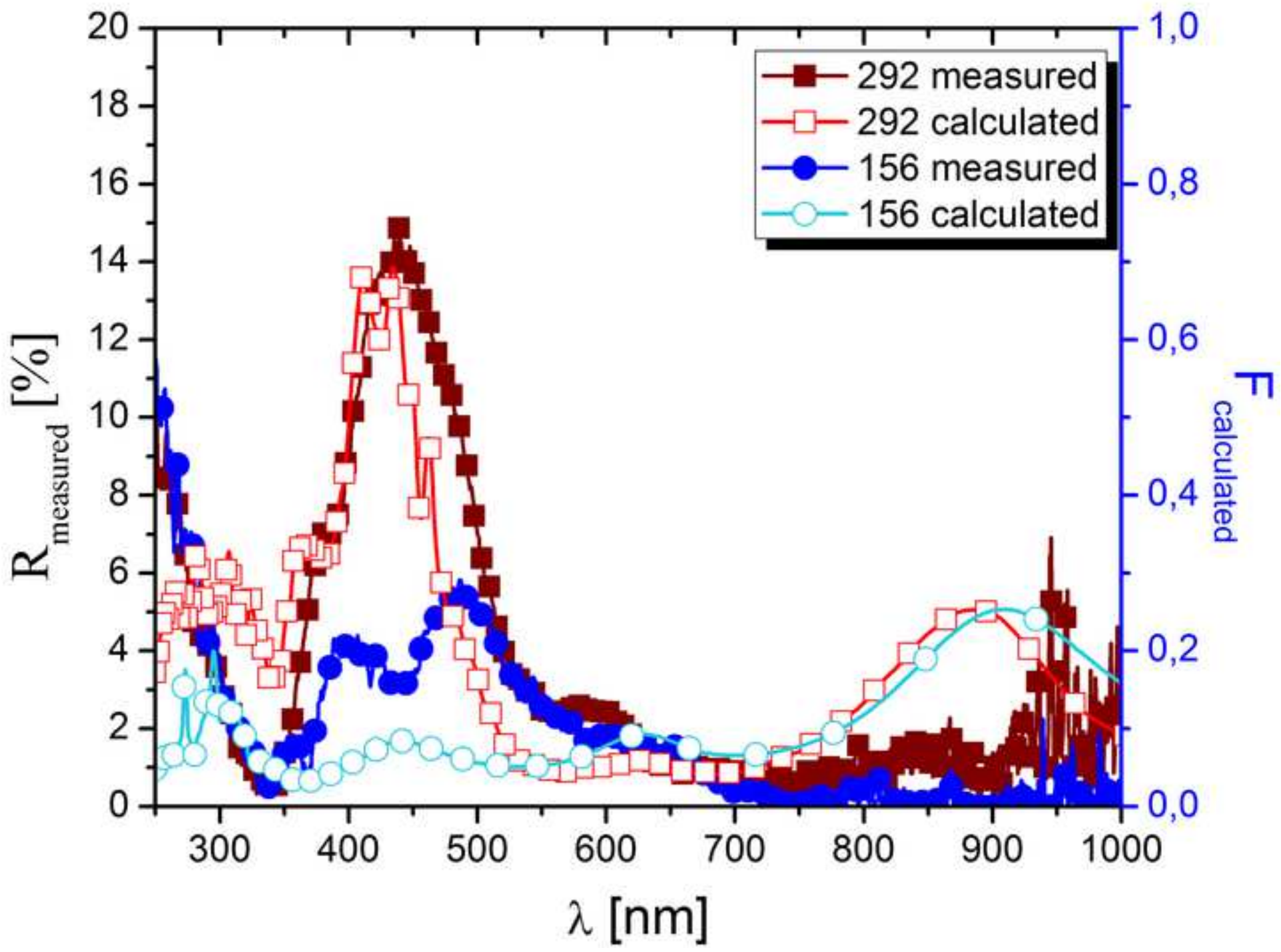
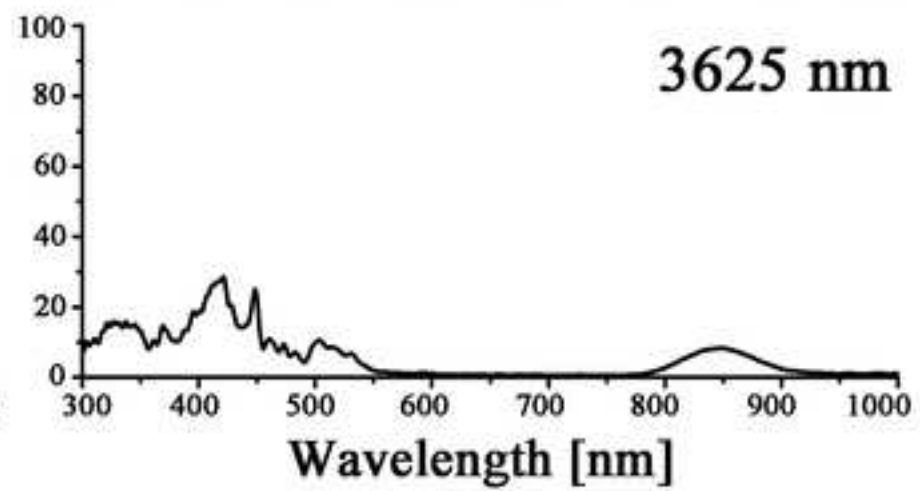
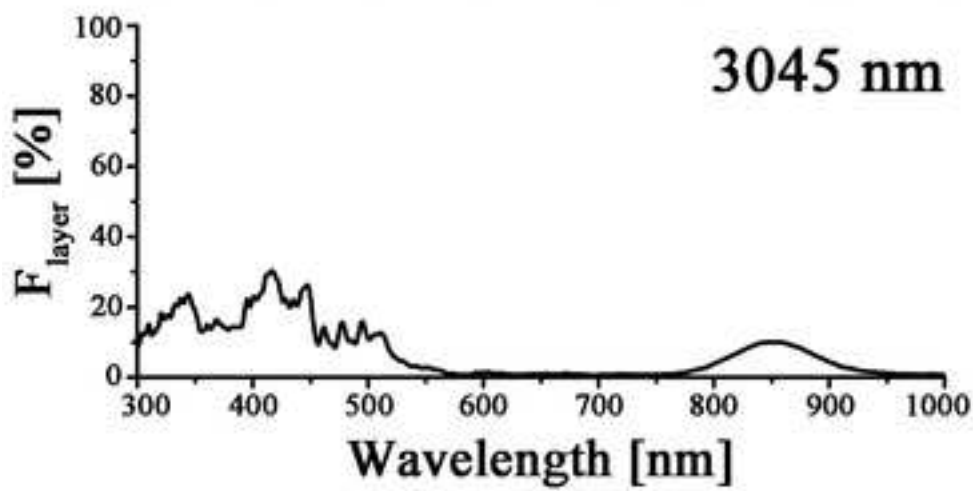
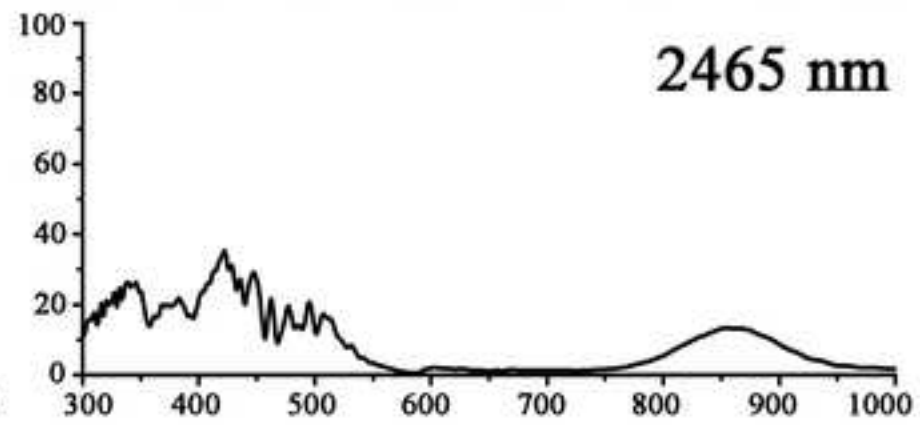
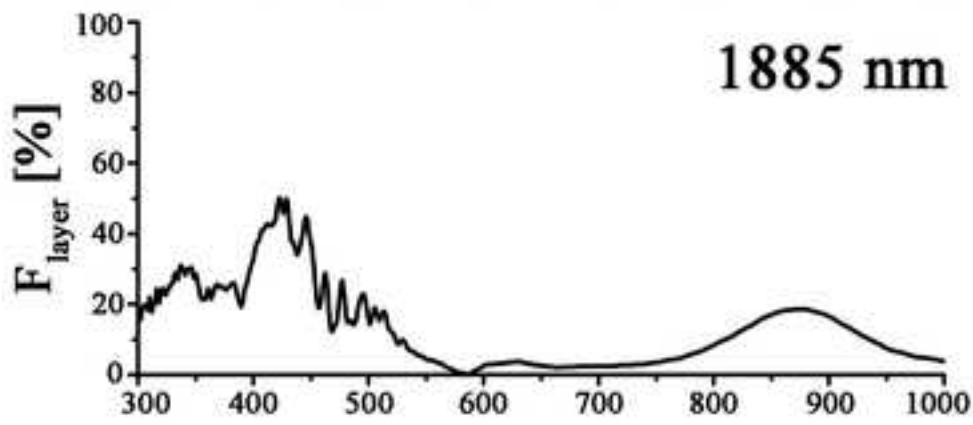
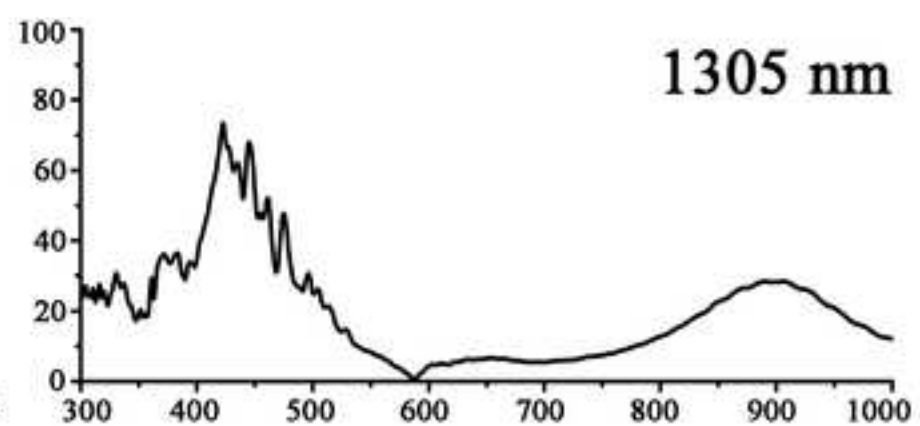
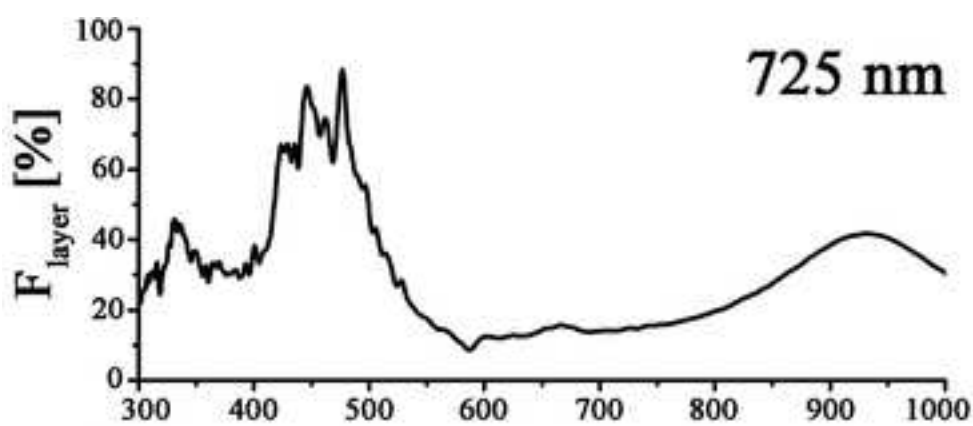


Figure9
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Wavelength [nm]

Wavelength [nm]

Figure10
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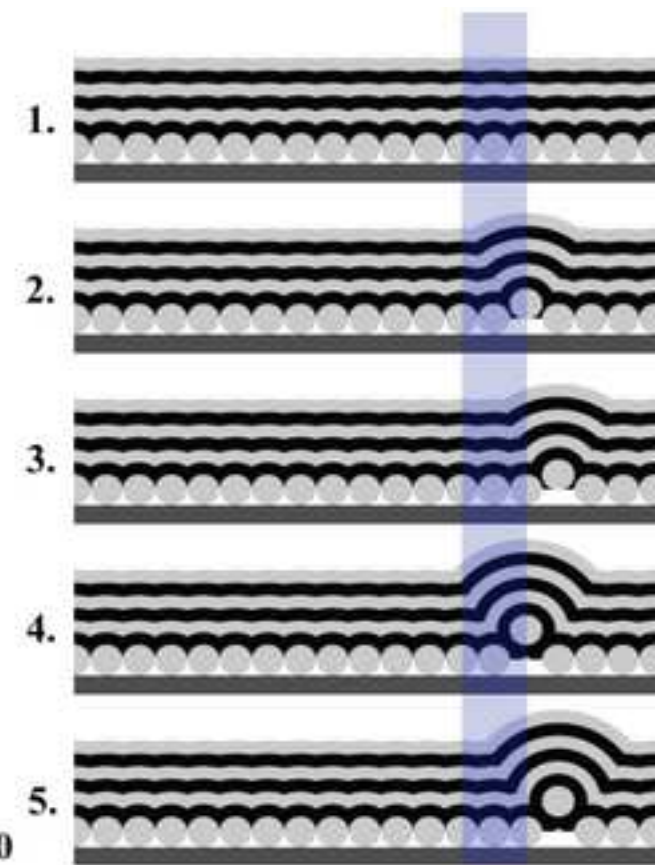
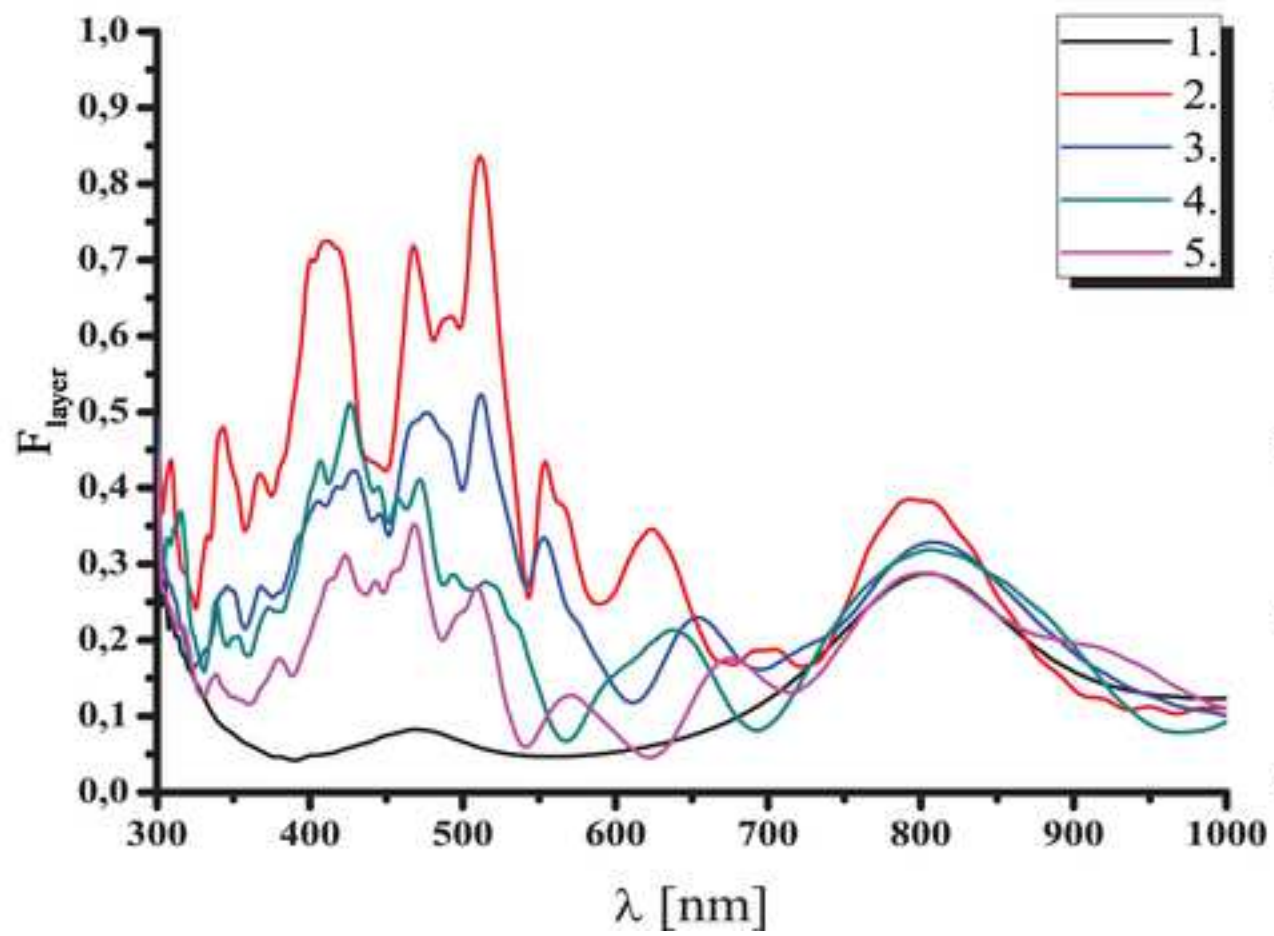


Table1

Spectral range	Refractive indexes			
	Wavelength	Si	SiO2	TiO2
300-410	388	6	1.47	2.64
410-480	435	4.85	1.47	2.55
480-620	531	4.16	1.46	2.44
620-1000	708	3.77	1.45	2.35