The modeling of the light sensitive titanium dioxide micro-rolls doped by noble metal nanoparticles

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Abstract
Titanium oxide films are photosensitive they have unusual optical properties. This article represents the possibility of the TiO objects (rolls) obtaining with predetermined optical parameters. The article also includes the comparison between numerical and physical experiments.

1. Introduction
The development and ordered distribution of metamaterial clusters/agglomerates is one of the prospective idea of nanotechnology in modern science. The self-assembly way of such structures synthesis is the most promising way for further investigations and fabrication. This kind of fabrication is well known and educated by many scientific teams all over the world [1-3].

Self-assembled nanostructures are well used in photonic applications. The determined optical response, controlled by geometry and structural features allows synthesizing metamaterial nano-micro-objects with properties matched with previously given ones. The development of synthesis methods of realization of spatially distributed nanostructures with controlled geometrical parameters is one of the most important goal of the modern nanophysics.

TiO2 is a very prospective material due to the unique physical properties and functionalities [4, 5], that is why nanostructures of the oxide are intensively studied in many laboratories worldwide.

Titanium oxides may demonstrate properties of metals and semiconductors due to the oxygen fraction. Such structures absorb light only in the narrow UV range effectively because of their huge energy band gaps. The enhancing of the light absorption may be achieved by doping obtained titanium structures by gold and silver nanoparticles. The adding of noble metals leads to a change of the dielectric permeability at optical frequencies, the variation of conductivity and other optical and electronic effects. The metamaterials consisted of TiO2 and metal NPs allows tuning their optical and electric properties.
2. Numerical modeling

Recently, much attention is paid to the study of the structure and properties of nanorolls of different composition and morphology. This article is devoted to the numerical modeling of titanium oxide structures and investigation of the dependencies of their absorption coefficients in the visible spectrum. The method of FDTD (Finite-Difference Time-Domain) was used for these calculations. This method was used for the numerical solution of Maxwell's equations. Such method is well implemented in the EMTL (Electromagnetic Template Library), so the computer modeling was carried out using the library.

During the construction of the numerical experiment using EMTL, the speed of light was assumed to be equal to one, which means the frequency of the electromagnetic wave $\nu = 1/\lambda$. The unit of time measurement is the time required by the light in order to pass the unit of length.

Numerical modeling begun with the construction of geometry. The computational volume was given as a parallelepiped using the coordinates of opposite angles. To simulate an infinitely remote plane wave source, the computational volume was divided into the areas of the common field and the scattered field. They were separated by a virtual boundary that serves to generate a plane wave in the region of the full field.

Perfectly Matched Layers (PML) were used as absorbing boundary conditions and were required to simulate the wave exit from the computational volume to infinity. They absorb all the waves falling on the boundary of the calculated volume, regardless of the angle of incidence. Periodic boundary conditions in one or more directions were used to model infinite periodic structures.

Detectors read the values of the fields and recorded their readings in binary files. Such detectors were used to measure the fields within the computational volume. At the end of the calculations, readable text files were created from these binaries.

Geometric objects were located in the calculated space. The material of the objects was determined by the dependence of the dielectric constant on the frequency, which can be set using the Drude – Lorentz model:

$$\varepsilon(\omega) = \varepsilon_\infty - \sum_{p=1}^{N_D} \sum \frac{\Delta \varepsilon_p \cdot \omega_0^2 p}{\omega^2 + i \gamma_p \omega} + \sum_{p=1}^{N_L} \sum \frac{\Delta \varepsilon_p \cdot \omega_0^2 p}{\omega_0^2 p^2 - 2 i \gamma_p \omega - \omega^2}$$

The parameters for members of the Drude and Lorentz plasma frequency $\omega_0$, damping $\gamma$, and the value of $\Delta \varepsilon$. The specified plasma frequency and attenuation had to be measured in radians per unit of time FDTD.

The calibrate function gives the values $\omega_0$ and $\gamma$ the required dimension, multiplying them by its argument. For some commonly used media, such as gold and silver, an approximation of the dielectric constant is already available in EMTL.

The simulated structure of titanium oxide nanorolls in this experiment is presented as a set of nested hollow cylinders of infinite length (fig. 1).

The input parameters are the thickness of the titanium oxide layers $h$ and the size of the gap between the layers $x$, which determines the twisting density. Based on these values, indicated in nanometers, the outer radius of the resulting nanoroll $R$ is calculated:

$$R = 660 + x + 3 h / 2.$$
According to the experiments, we had to add gold and silver particles. These inclusions were defined in the form of spheres of a given radius, which were placed in different proportions and with a given concentration in the layers of the nanoroll (fig. 2). To place one object inside another, the priority value of its environment must be higher than properties of the object, which it is superimposed.

3. The physical experiment and comparison
The experimental part of the article includes the deposition of the titanium oxide thin film on a cold substrate by spray-jet method and placing it between constant magnets. The addition of gold and silver (volume ratio 1:1) particles using droplet deposition, have resulted in penetration of noble metal particles (average diameter was about 10 nm) inside the titanium oxide thin film (TiO) and became a doping component of the system. After we had moved the sample far from magnets (removing magnetic field) the thin film started to roll in scrolls, in that case we have obtained titanium oxide scrolls doped by noble metals (average diameter was about 2 μm). The absorption properties of resulted structure were studied.

To compare the experimental and theoretical absorption spectra of obtained structure we have used the popular graphics program Gnuplot to build graphs based on EMTL output text files (fig. 3).
Fig. 3. The absorption spectra of titanium oxide rolls doped by gold and silver nanoparticles

The resulting comparison spectra of obtained structure allows us to investigate the influence of doping component and experimental conditions on the final spectra of absorbance (the quantity of doping component, the ratio of components, the thickness of obtained film etc.).

Conclusion
Small differences and high correlation between experimental and theoretical spectra prove the correctness of computer modelling and allow to determine optical properties of obtained structure previously instead of empirical data collecting.

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