Enhancement of the photocatalytic activity of nanoparticles due to the localization of electromagnetic fields

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Abstract. In this work, we consider the designs of nanoparticles based on titanium dioxide. We focus on localizing energy in the near-surface layer of particles in order to increase the generation of electron-hole pairs in this region. This should result in an enhancement in their photocatalytic activity.

1. Introduction
Photocatalysis is the process of acceleration in the rate of a chemical reaction that occurs due to the generation of electron-hole pairs under electromagnetic irradiation. It can be used in solving topical issues, for example, among applications of photocatalysis there are water and air purification in industry [1], sterilization in medicine [2], hydrogen production in energetics [3].

The efficiency of photocatalysis depends on many parameters. Some of them are determined by the material that is used as a photocatalyst. For example, recombination rate or diffusion length of electrons and holes. Other parameters depend on the geometry of the photocatalyst. The most important parameter among others is the contact area between the photocatalyst and the environment and the percentage of the light absorbed in the active region. One of the most popular materials to create a photocatalyst is titanium dioxide because it has a number of advantages: low cost and high accessibility, non-toxicity, and photoreactivity. At the same time, the bandgap width of TiO2 corresponds to the UV region of the spectrum, which limits its applicability under solar irradiation. Numerous approaches were proposed to increase its sensitivity to the visible range and to improve other parameters of the material such as crystal structure control, photosensitization with dyes [4], metal and non-metal doping [5], creation of heterostructures [6], surface decoration [7] and many others. The materials science side of the problem has already been explored quite well. But there is another important and less studied drawback of photocatalysts, which is that the light is absorbed outside of the active region. If electrons are generated at the center of a particle, then there is a high probability that they will recombine and will not contribute to photocatalysis. For example, for TiO2 the diffusion length of minor carriers - holes is about 10 nm. Then it is logical to consider the generation of carriers in the area that is located at this distance from the surface.

There were published a few papers, which declare localization of electromagnetic fields connected with multipoles excitation for magnetic field separation [8], scattering maximization
and amplification [9], localization of field in biological particles [10], light driven nanomixing [11].

Active all-dielectric nanophotonics researchers were also applied to photocatalysis. In the 2020 study [12] anapole excitation in TiO2 cylinders was suggested to increase the rate of Ag reduction. There were also studies related to the plasmonic enhancement of the fields [13].

However, localization of the energy inside of the particle doesn’t lead to the photocatalytic activity enhancement if it occurs not in the active regions that we pointed out above. And that’s why in this research we concentrated on the ability of particles to localize energy inside of the pre-surface layer with 10 nm width.

2. Results
In this work, we carried out numerical simulations for nanoparticles with the addition of titanium dioxide of various geometries. We started from the bulk TiO2 cylindrical nanoparticles as discussed in [12]. For the objective function we used the value of the electromagnetic energy inside of the 10 nm layer, divided by the value of the energy in the volume of the water with the same size:

$$W_{\text{norm}} = \frac{\text{Re}(\varepsilon_{\text{TiO2}})}{4} \left( \int_{V} |E(r)|^2 d^3r \right) V_{10[nm]} \frac{1}{2} \varepsilon_{\text{water}}$$

(1)

![Figure 1](image1.png)  
**Figure 1.** Distribution of normalized energy within 10nm pre-surface layer depending on the size parameters of TiO2 cylinder

![Figure 2](image2.png)  
**Figure 2.** Distribution of normalized energy within 10nm pre-surface layer depending on the size parameters of Si@TiO2 cylinder

The obtained results are represented in figure 1. It shows multiple enhancement regions. For small height and large radius, electromagnetic filed configurations corresponding toroidal moments are localized in the vicinity of interface TiO2/solution. That rises photocatalysis enhancement and it was addressed in the paper [12] to the anapole states. It should be noted that the existence of an anapole state is not a requirement for the reaction acceleration. Photocatalytic reactions could be driven by basic multipoles (this definition was well described in the paper [14]. Significant field photocatalytic reaction acceleration is found for high cylinders with fairly low radius. Those regions are characterized by the combination of toroidal and basic moments in the scattering spectrum, which in sum shows better amplification rather than anapole-driven regions. In addition, layered structures with addition of Si were modeled (fig.2). It can be seen from obtained distribution that in the presence of a material with higher index the maximum
value of the objective function has increased. A similar effect is observed for other considered geometries, for example, cones.

3. Conclusion
To conclude we examined the ability of nanoparticles to concentrate energy inside the subsurface layer to apply this effect in photocatalysis. It has been shown that it is possible to improve the existing results for anapole states, since the concentration should appear in certain regions. This work shows that photocatalysis is an attractive research area, where the use of already obtained knowledge about the optical responses of dielectric nanoparticles can lead to significant results.

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