

Preparation and photocatalytic activity of TiO₂ photonic crystals modified by bimetallic Ag-Pt nanostructures

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Supplementary information

Scanning electron Imaging (SEM)

Porous TiO₂ coatings with a disordered arrangement of pores were obtained using a mixture of 3 different sizes of PS microspheres - 300 nm, 460 nm and 600 nm in a ratio of 1:1:1. The morphology of the obtained coatings is shown in Fig. S_1. It can be seen that this structure consists of pores with a diameter corresponding to the diameters of PC300, PC460 and PC600, but due to the polydispersity it is not ordered and does not have a characteristic hexagonal structure. Due to the lack of order, the generated metallic nanostructures are less noticeable than in the case of ordered coatings. However, as in the case of photonic crystal modifications, AgNSs are visible in the form of clear, spherical islands, and PtNSs as very small particles covering the surface of TiO₂.

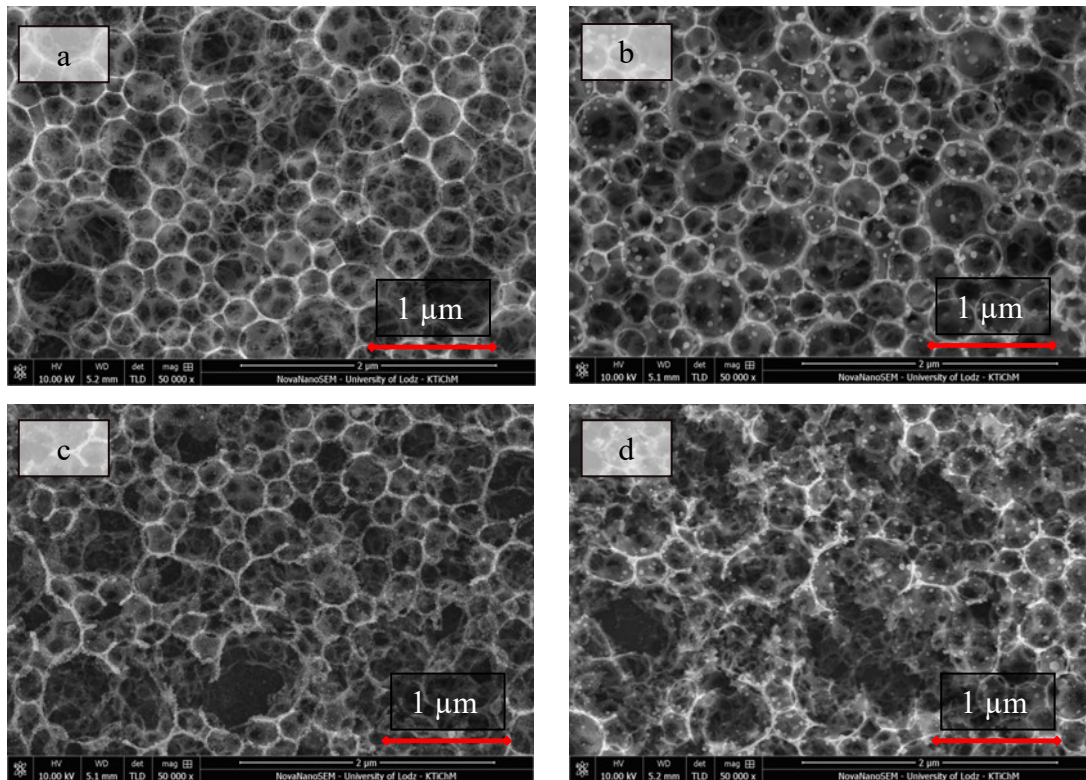


Fig. S1. SEM images of non-photonic crystals (NPC): (a) pristine NPC; (b) AgNSs/NPC; (c) PtNSs/NPC and (d) AgPtNSs/NPC.

In order to assess the effect of the structure of the TiO₂ photonic crystal on its photocatalytic properties, non-porous, solid reference coatings were prepared for comparative purposes, for which CCT polystyrene matrices were not used - Fig. S2 (a). It can be seen that the produced coating is not porous and its surface is smooth. The generated AgNSs are visible in SEM images as bright objects, mostly of regular spherical shape - Fig. S2 (b, c). On the other hand, PtNSs form characteristic fine-grained structures Fig. S2 (d, e). In the case of the composite system consisting of a combination of silver and platinum, both metals are visible on the TiO₂ surface, with larger silver nanostructures and platinum nanostructures covering them Fig. S2 (f, g).

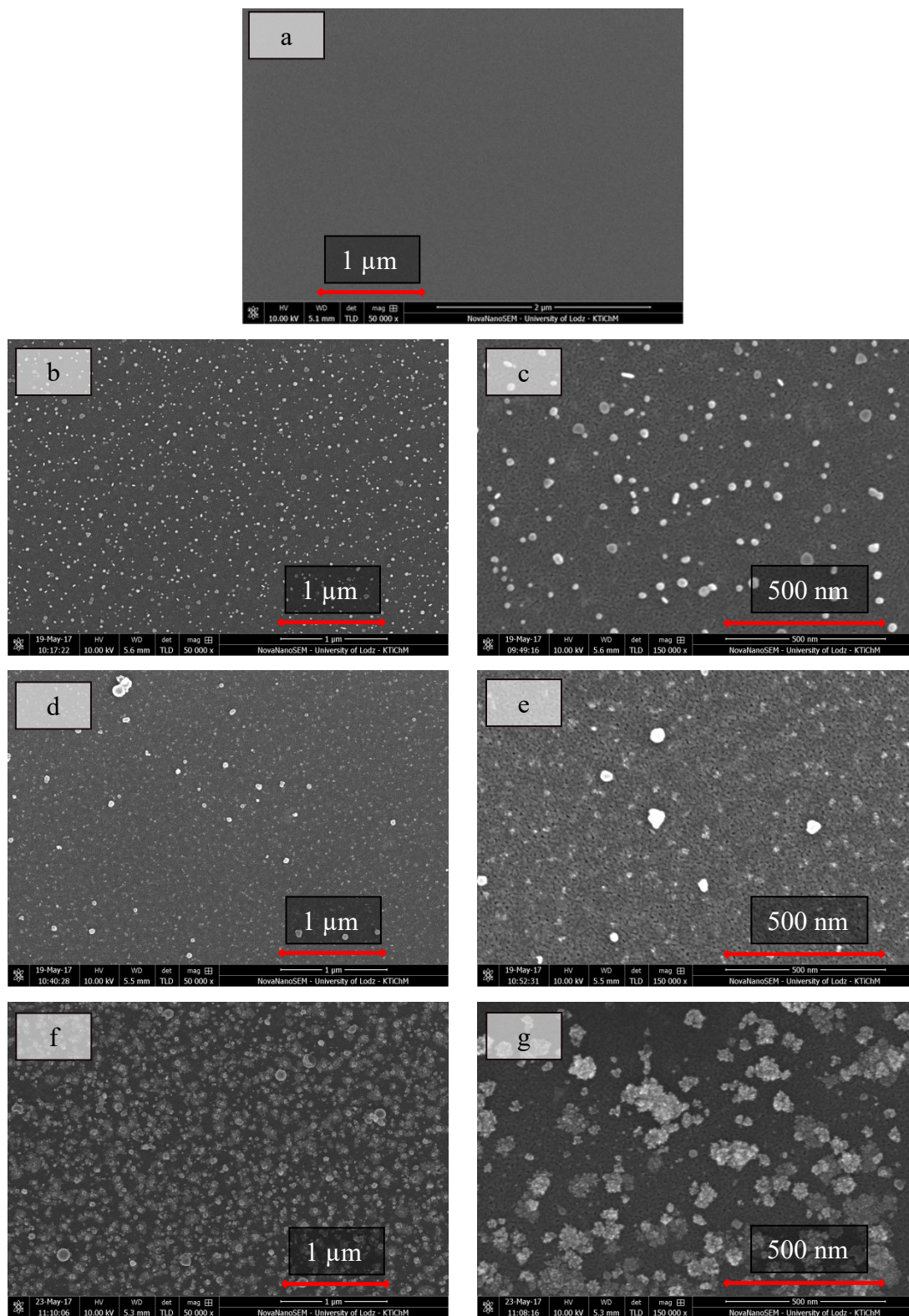


Fig. S2. SEM images of non-porous solid coatings: (a) pristine TiO_2 ; (b, c) $\text{AgNSs}/\text{TiO}_2$; (d, e) PtNSs/NPC and (f, g) $\text{AgPtNSs}/\text{NPC}$.

High-angle annular dark-field imaging (HAADF)

The obtained elemental maps for titanium and oxygen overlap, which proves that the PCs structure is built of these elements – Fig. S3 (b, d). Moreover, low and high intensity signals on the Ag map correspond to very small particles distributed over the whole porous scaffold and to larger AgNPs that are visible on its surface at the bottom part of Fig. S3 c.

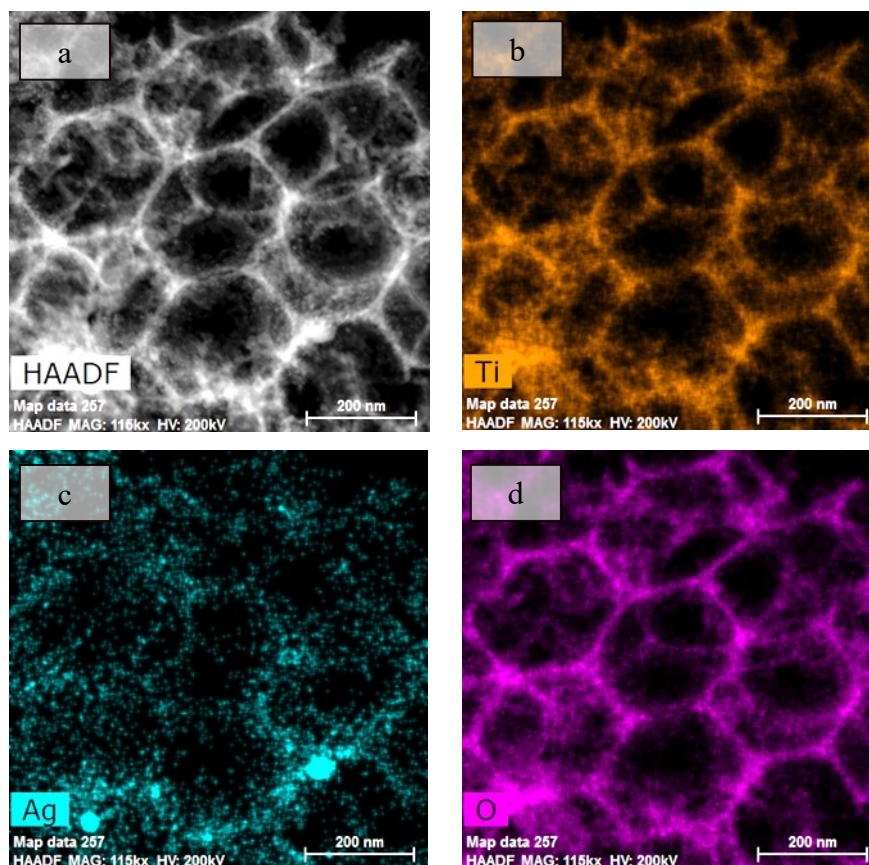


Fig. S3. HAADF images of: (a) AgNSs/PC300 and elemental maps of: (b) Ti; (c) Ag and (d) O.

In the case of the platinum-modified photonic crystal, the superimposition of the elemental maps for Ti and O (Fig. S4 b, d) and the coverage of the PC surface by platinum nanostructures are also visible - Fig. S4 c.

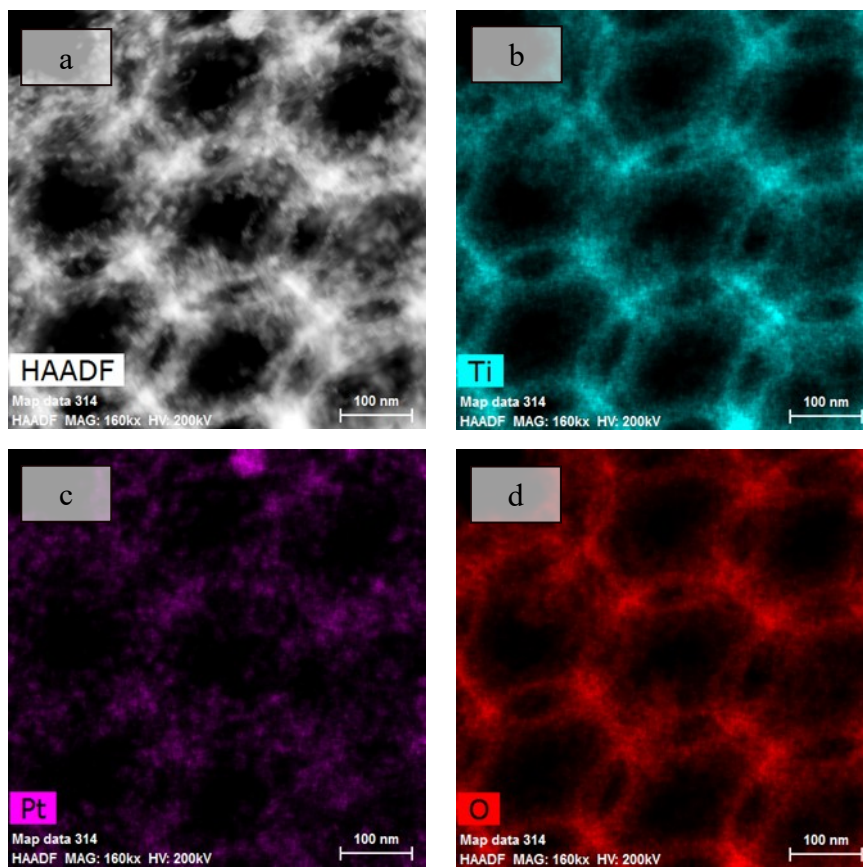


Fig. S4. HAADF image of: (a) PtNSs/PC300 and elemental maps of: (b) Ti; (c) Pt and (d) O.

Atomic force microscopy imaging

The topography of the polymer template built of PS beads having the diameter 300 nm and corresponding structure of TiO₂ photonic crystal were also investigated with the use of AFM technique. Obtained results were similar to those obtained with the use of SEM. Moreover, it was found that the pore size of resulted photonic crystals correspond to the size of applied PS beads. AFM images of PS template and corresponding photonic crystals are presented in Figs. S5 and S6, respectively.

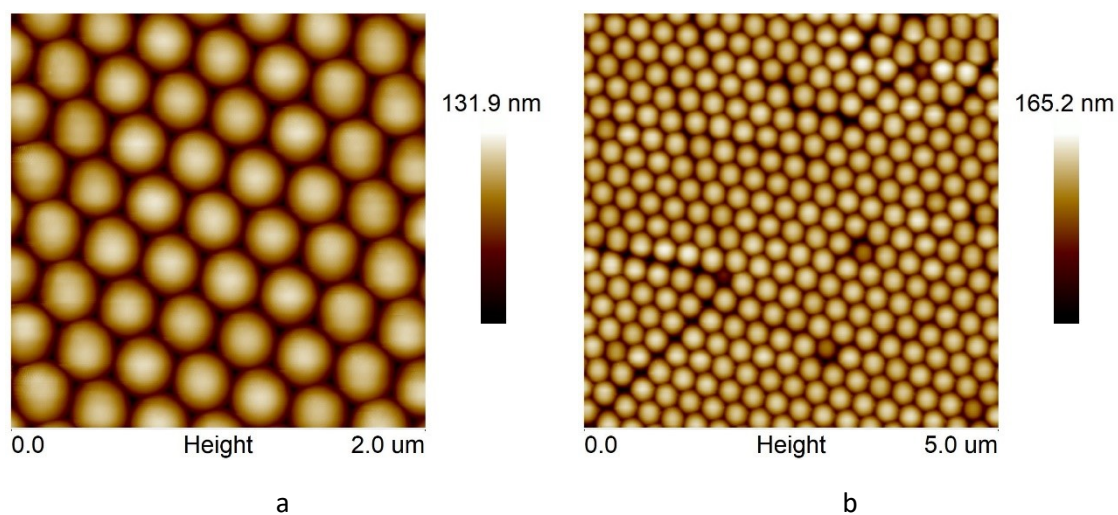


Fig. S5. AFM images of PS beads 300 nm: (a) 2 nm × 2 nm and (b) 5 nm × 5 nm.

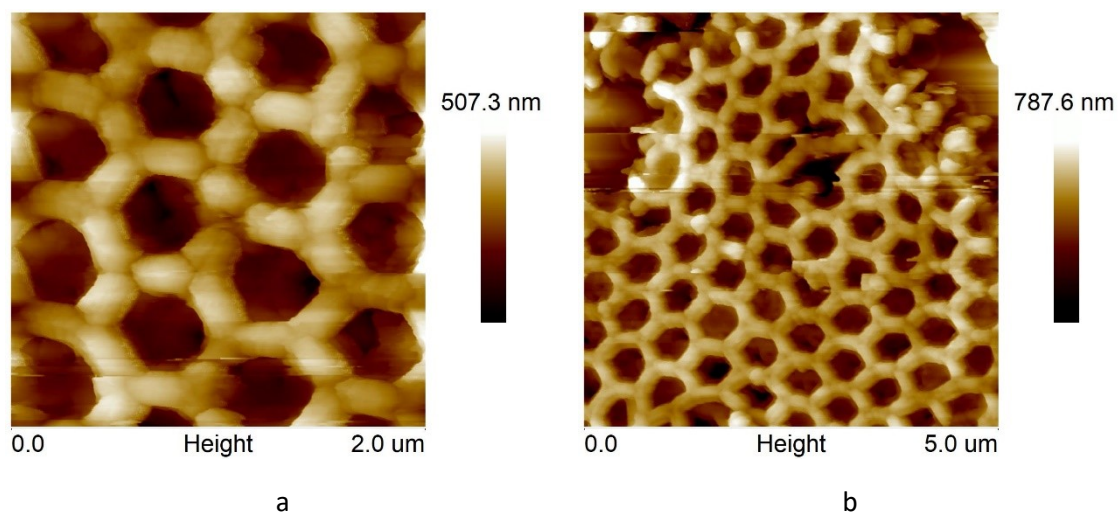
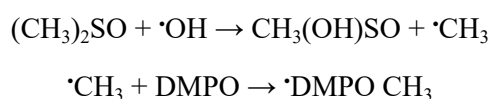


Fig. S6. AFM images of TiO₂ PC300: (a) 2 nm × 2 nm and (b) 5 nm × 5 nm.

Investigations of the influence of structure on the amount of hydroxyl radicals generated in the TiO₂ photonic crystal

In order to investigate the influence of the TiO₂ photonic crystal structure on the efficiency of hydroxyl radical generation, electron paramagnetic resonance (EPR) spectroscopy was used. This technique allowed for the comparison of the amount of $\cdot\text{OH}$ radicals that were generated as a result of irradiation of non-porous, solid TiO₂ and the TiO₂ PC300 photonic crystal. It is known that hydroxyl radicals are one of the factors responsible for the decomposition of organic substances (if the decomposition reactions take place with their participation). The photocatalytic efficiency of the obtained coatings depends on their quantity.

The tested photonic crystals were exposed to UV radiation in the presence of dimethyl sulfoxide (DMSO), which reacted with $\cdot\text{OH}$ radicals and resulted in methyl $\cdot\text{CH}_3$ radicals, which were then trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO):



Due to the very short lifetime of hydroxyl radicals, direct recording of their spectra is very difficult or even impossible. Therefore, the use of a trapping agent in the form of DMPO is necessary. Methyl radicals obtained in the reaction with DMSO react with DMPO, which allows obtaining a characteristic 6-peak signal typical of $\cdot\text{DMPO-CH}_3$ radicals in the EPR technique.

Fig. S7 shows the obtained EPR spectrum of $\cdot\text{DMPO-CH}_3$ radicals generated in the presence of PC300 and solid TiO₂. Although this technique does not allow for an exact determining the amount of generated hydroxyl radicals it allows for estimation of their differences by comparing the intensity of the spectra. From intensity obtained signal, it can be clearly concluded that the photonic crystals generate more $\cdot\text{OH}$ on their surface. In consequence they exhibit higher photocatalytic activity than solid TiO₂ coatings. The generation of larger amount $\cdot\text{OH}$ radicals can be attributed to more efficient processes of production of reactive oxygen species due to the slow photon effect.

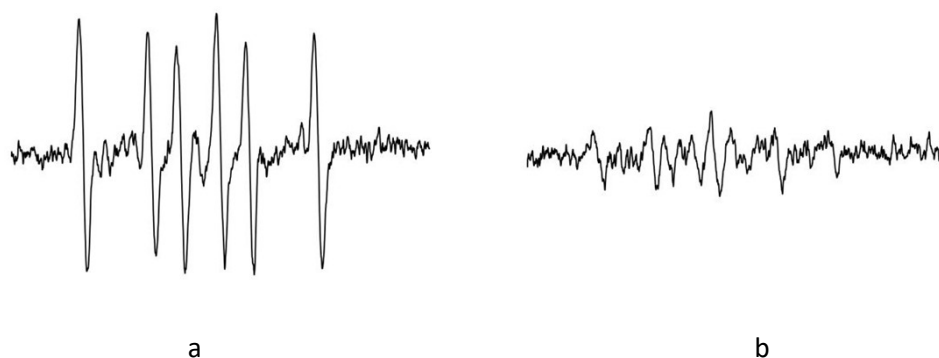


Fig. S7. EPR spectrum of $\cdot\text{DMPO-CH}_3$ radicals generated in the presence of PC300 (a) and solid, non-porous TiO₂ (b).

Investigations of the crystallographic structure based on X-ray spectra

Crystallographic structure of TiO_2 , the main component of the crystal photonic, was identified using X-ray diffraction (XRD). Fig. S8 shows the XRD spectrum of the PC300 crystal showing peaks at: 25.32° (101), 37.98° (004), 48.02° (200) corresponding to the structure of anatase TiO_2 .

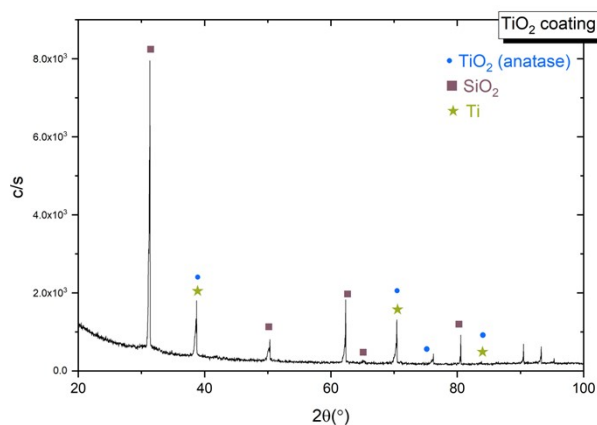


Fig. S8. XRD pattern of PC300 TiO_2 coating.

The XRD pattern shows characteristic peak position values. TiO_2 photonic crystals prepared by the research group supervised by Zheng *et al.** have also studied for their crystallographic structure with application of XRD techniques. The spectrum they obtained showed peaks at 25.3° (101), 37.9° (004) and 48.1° (200). From these results it can be concluded that preparation of TiO_2 in the form of photonic crystal does not affect its crystallographic structure.

* - X. Zheng, S. Meng, J. Chen, J. Wang, J. Xian, Y. Shao, X. Fu, D. Li, Titanium Dioxide photonic crystals with enhanced photocatalytic activity: Matching photonic band gaps of TiO_2 to the absorption peaks of dyes, *J. Phys. Chem.-US* 117 (2013) 21263 – 21273.