

Photochromic properties of TiO₂: doping effect

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Abstract. TiO₂ is one of the most studied photoactive materials (photocatalyst, photochromic agent). Improving photochromic characteristics includes not only increasing the intensity of photocoloring but also increasing the speed of coloring/bleaching as well as the cyclicality of the process. This can be done by changing the structure of the material (doping, phase transformations, creating heterojunctions). This report presents spectrophotometric studies of the effect of doping on the photochromic properties of titanium dioxide phase brookite. The doping process was carried out by exposing a low-temperature plasma of an underwater diaphragm discharge to a TiO₂ sol where the precursors of doping elements were electrode materials. Visible spectroscopy results demonstrate the influence of the doping process and dopant material on the photochromic properties of titanium dioxide.

Keywords: TiO₂, doping, photochromism.

1. Introduction

Titanium dioxide is widely known as a photocatalyst despite the fact that TiO₂ has a wide band gap (3.0–3.2 eV) [1]. Among the physical and chemical methods for producing TiO₂, one can distinguish the sol-gel method, which allows one to obtain an oxide of a given structure (anatase, rutile), size of particles, and textural properties [2]. To increase the photocatalytic properties under the action of visible light, the doping method is used [3]. Along with photocatalytic properties, titanium dioxide also has photochromic properties [4]. The main problem with using TiO₂ as a photochromic material lies in the low rate of coloring-bleaching processes under the influence of light. Photochromic properties can be improved by creating binary structures, doping, and creating composites based on polymers and oxide structures. Currently, Ag, Cu, Mo, Nb, V, and W as ions and oxides are being intensively studied as doping agents that increase the photochromic characteristics of titanium dioxide. As a doping method, the use of low-temperature plasma is the most promising [5]. In this case, the electrode material acts as a source of ions or oxide structures. This paper examines the effect of doping on the photochromic properties of titanium dioxide. As a doping method, the path of exposure to a low-temperature plasma of an underwater discharge of the diaphragm type was chosen. Mo, Nb and W were used as doping agents. The choice is due to the well-known photochromic properties of the oxides of these metals.

2. Experimental

TiO₂ was prepared using sol-gel technology. Dissolve 4.5 g of polyvinylpyrrolidone (PVP) in 100 mL of distilled water heated to 80 °C. Next, add 6 g of citric acid and stir until completely dissolved. After adding 2.5 ml of titanium isopropoxide, heating stops. The synthesis proceeds for 48 hours. Complete dissolution of the white flakes and clearing of the solution indicate the end of the process.

An underwater diaphragm discharge was excited in the volume of liquid sol from an alternating current source. Two metal electrodes were immersed in a volume of liquid. One of them was placed in a quartz ampoule with a small hole (diaphragm). The diaphragm diameter was 2 mm. Molybdenum, niobium, and tungsten wires with a diameter of 0.8 mm were used as metal electrodes. Processing time was 90 s. A more detailed method of plasma treatment of sol is discussed elsewhere [3].

The phase composition of the sol particles were studied using Raman spectroscopy (Confotec NR500 microscope, excitation laser with $\lambda = 532$ nm) in the range of 100–1000 cm⁻¹. The

photochromic effect was studied by irradiating sols before and after plasma treatment with a 15 W UV lamp (NDTRADE LLC) with a wavelength of 365 nm. Absorption spectra in the visible region (400–900 nm) were registered using a SF 56 spectrophotometer.

3. Results and Discussion

During the combustion of the diaphragm discharge, the electrodes are sputtered. This is evidenced by a change in the mass of the electrodes (1.5 mg, 1.2 mg, and 0.5 mg for Mo, Nb, and W, respectively). Fig. 1 shows Raman spectra of TiO₂ sols before and after plasma treatment. The bands in the region of 100–850 cm⁻¹ belong to titanium dioxide phase brookite [6]. The bands at 899 and 935 cm⁻¹ are attributed to PVP [7]. Plasma treatment does not result in the appearance of new bands, but does cause a shift in the main bands. This indicates the incorporation of metal ions into the structure of TiO₂ and the absence of oxide phases on its surface [8].

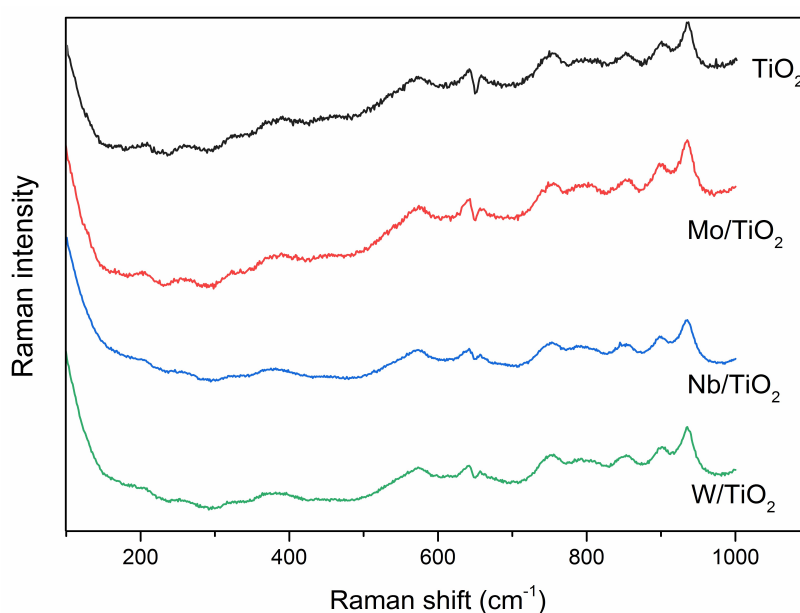


Fig. 1. Raman spectra of undoped and doped TiO₂ sols.

The absorption spectra of photocolored titanium oxide sols are presented in Fig. 2. The absorption maximum is clearly visible in the region of 530–540 nm, as well as an unresolved band centered at 650 nm. All these absorption bands are attributed to their own F color centers. This is inherent in an external defect arising from oxygen vacancies that have captured two electrons [9, 10]. It was noted that the doping process shifts the absorption maximum to longer wavelengths. This is typical for structures of doped titanium dioxide [9]. The results of spectral studies showed that the doping process increases the color intensity. At the same time, a pattern was noted in the intensification of color in the series: TiO₂<W/TiO₂<Mo/TiO₂<Nb/TiO₂ (Fig. 3). The highest intensity of photocoloring in the case of niobium doping can be explained by the formation of Ni⁵⁺–Ti³⁺ defect pairs in the crystal lattice during the doping process [11].

Studies have shown that photocoloring occurs quickly and after 10 minutes of irradiation the color intensity does not change (Fig. 4a). And doping process accelerates the photocoloration. The discoloration process is slower (Fig. 4b). 50% color loss occurs within 3 hours and complete discoloration is recorded after 20 hours for doped structures and after 24 hours for undoped TiO₂.

Despite the rather long bleaching time (20 hours), the result obtained is the best in comparison with published data. Previously, it was found that W⁶⁺/TiO₂ structures discolor in 24–26 hours [8] and Mo⁶⁺/TiO₂ in 3 days [12].

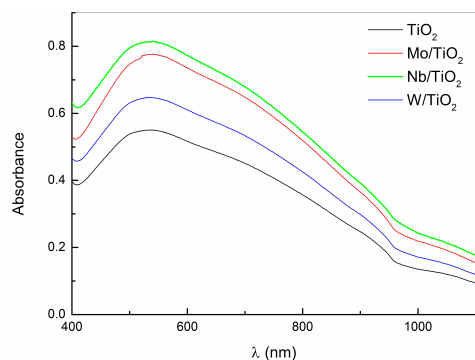


Fig. 2. Absorption spectra of irradiated sol before and after plasma treatment.

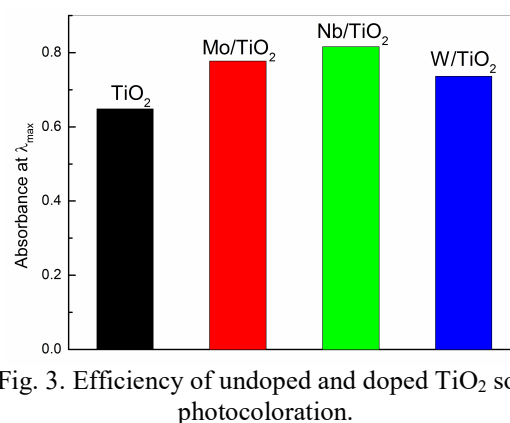


Fig. 3. Efficiency of undoped and doped TiO₂ sols photocoloration.

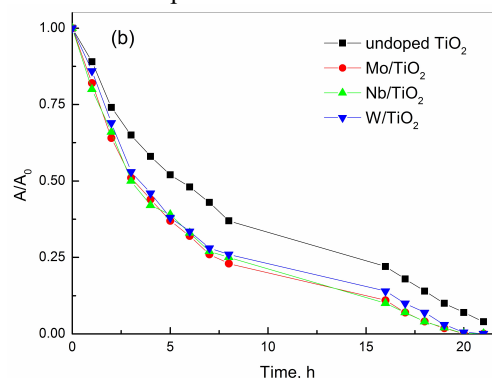
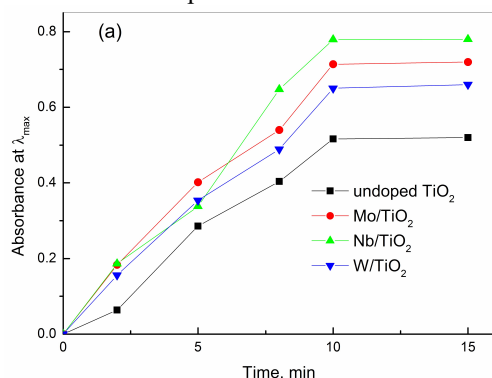


Fig. 4. Kinetics of photocoloration (a) and dynamic of bleaching (b) TiO₂ sols before and after plasma treatment

The reason for this may be the plasma modification of sols, the phase composition of titanium dioxide, as well as the degree of oxidation of the doping agent. Previously published data presented studies of the photochromic properties of TiO₂ with the structure of anatase, amorphous anatase or mixed-phase oxide (anatase, brookite, rutile) [4, 8, 9, 13]. This work presents the photochromic properties of the brookite phase. On the other hand, the oxidation state of the doping agent can also affect the photochromic properties. In general, photochromicity can be described as follows. When irradiated with light, an electron and a hole are formed, which accumulate in the conduction band or participate in redox processes. If the TiO₂ matrix contains doping agents in maximum degrees of oxidation (for example, W⁶⁺, Nb⁵⁺, or Mo⁶⁺), only photogenerated electrons participate in the redox process. In this case, electrons are delocalized near the excess positive charges of dopant ions and have less affinity to participate in oxidation reactions (bleaching process) [11]. In the case of the presence of non-stoichiometric oxides, in which Me⁶⁺–Me⁵⁺ states exist, both a photoelectron and a photohole participate simultaneously in the oxidation-reduction process. It was previously established that the action of an underwater diaphragm discharge leads to the formation of structures of non-stoichiometric oxides of tungsten and molybdenum (W₁₈O₄₉, Mo₄O₁₁) [14]. This may be the reason for both increased coloring and accelerated discoloration (oxidation).

4. Conclusion

The photochromic properties of TiO₂ in the brookite phase were studied for the first time. Doping titanium dioxide with d-metal ions through an underwater diaphragm discharge leads to an improvement in its photochromic characteristics, which is expressed not only in increasing the intensity of photocoloring but also in increasing the rate of bleaching.

Acknowledgements

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5. References

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