

Role of Iron and Chromium in the Photocatalytic Activity of Titanium Dioxide Films on Stainless Steel

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Abstract—Photocatalytically active titanium dioxide films have been formed on stainless steel grids via sol–gel process followed by heat treatment in the temperature range of 450–550°C. During UV irradiation of the films in an aqueous solution of the Rhodamine B dye and in distilled water we have detected iron and chromium dissolution from uncoated grid regions and the deposition of iron and chromium compounds onto the titanium dioxide surface. The deposition rate of these compounds increases with annealing temperature, which leads to a decrease in the photocatalytic activity of the films.

Keywords: titanium dioxide, stainless steel, sol–gel method, nanoparticles, photocatalysis, Rhodamine B

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INTRODUCTION

Environmental pollution as a result of anthropogenic activities causes long-term damage to the ecosystems of water bodies and has a negative effect on the availability and quality of drinking water. Organic pollutants are a particularly serious problem because they are resistant to standard water treatment technologies [1]. Therefore, more and more attention is being given to the development of effective approaches for removing organic pollutants. One such approach is photocatalytic decomposition. This method utilizes the energy of solar light, which upon absorption by a semiconductor material placed in an aqueous medium causes the formation of •OH radicals near its surface. These radicals are highly oxidative towards organic compounds [2].

One of the most attractive photocatalytic materials, which combines high effectiveness, mechanical durability, chemical and thermal stability, and a relative environmental friendliness, is titanium dioxide (TiO₂) with the anatase structure—a semiconductor with a band gap of 3.2 eV [3]. This accounts for the increased research interest in TiO₂-based nanostructures [4–7]: owing to their large surface area, they exhibit high photocatalytic activity. The highest purification rate is achieved by using TiO₂ nanoparticles, however, due to the difficulty of their extraction from water, preference is increasingly being given to TiO₂ films on various substrates [8–10].

Stainless steel successfully meets the requirements for substrates for TiO₂: low cost, high strength, and chemical and thermal stability. TiO₂ films have been

formed on stainless steel substrates by sol–gel method [11–13], electrophoresis [14], chemical vapor deposition [15], and self-organization during evaporation [16]. There is experimental evidence that such structures possess high photocatalytic activity for hydrogen generation [14] and decomposition of organic compounds [15, 16]. Assuming that Fe₂O₃ (a semiconductor with a band gap of 2.2 eV [17]) is formed at the film/substrate interface in the process of inevitable heat treatment for the preparation of TiO₂ with the anatase structure, it is of great current interest to gain insight into the role of iron and its oxides in the photocatalytic activity of TiO₂ films grown on stainless steel substrates.

The purpose of this paper is to assess the effect of iron, chromium, and nickel—the major components of stainless steel substrates—on the photocatalytic activity of nanostructured TiO₂ films produced by sol–gel method.

EXPERIMENTAL

As substrates for TiO₂ growth, we used Kh17N8 chromium–nickel stainless steel grids with a wire diameter of 0.5 mm and an a pitch of 3 mm, which were cut into squares with eight wires on each side. The steel surface preparation procedure included washing in isopropanol, a 5% NaOH solution, and distilled water.

TiO₂ films were formed on the surface of the steel grids by sol–gel method. Ti-containing sol was prepared by mixing 9.4 g of ethanol, 9.4 g of butanol,

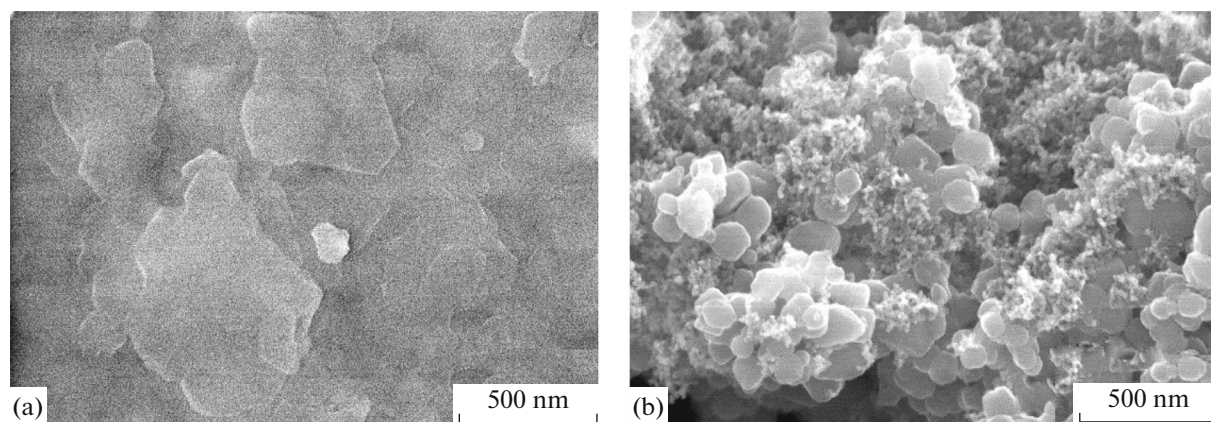


Fig. 1. Stainless steel wire surface: (a) chemically cleaned surface, (b) TiO_2 film deposited by sol–gel method followed by heat treatment at 500°C .

0.32 g of acetylacetone, 1.56 g of titanium tetraisopropoxide, and 1 g of water. Next, to the resultant sol was added 0.2 g of sulfuric acid, 0.67 g of submicron-sized TiO_2 particles, and 0.67 g of P90 TiO_2 nanoparticles (Evonik). The resultant mixture was homogenized by grinding in a ceramic mortar until stable suspension was obtained. The sol was deposited on the surface of the grids by immersion for 1 min. Next, the grids were withdrawn from the sol, thoroughly shaken to remove suspension excesses from the wire intersection regions, and dried at 200°C for 5 min in air. The immersion–drying cycle was repeated five times. The grids were then heat-treated at 450, 500, or 550°C for 30 min in air. The films thus produced were of the order of $3\ \mu\text{m}$ in thickness.

The surface structure of experimental samples was examined by scanning electron microscopy (SEM), and the elemental composition of their surface layer was determined by energy dispersive X-ray (EDX) analysis.

The photocatalytic activity of the structures obtained was assessed from the bleaching of Rhodamine B in an aqueous solution at room temperature. To this end, 3 mL of the Rhodamine B solution (concentration of 13 mg/L) and a sample were placed in a Petri dish and left to stand for 30 min in order to equilibrate dye adsorption and desorption processes. Next, the system was exposed to ultraviolet light. The light source used was an 8 W gas-discharge mercury lamp with a filter separating out light at the wavelength of 365 nm. The lamp was placed 1 cm from the surface of the solutions being irradiated. In the course of irradiation, the Petri dishes were secured to a platform of a laboratory shaker, which moved along a circle of 4.5-mm radius at 180 rpm. This ensured effective agitation of the solutions. Every 20 min of irradiation, we took a 2-mL portion of the solution and measured its absorption spectrum in the wavelength range of 400–700 nm on a Proscan MC 121 spectrophotometer. After that, the portion was returned

to the solution and irradiation was continued. The residual Rhodamine B concentration was determined using a premeasured calibration plot of the absorbance of Rhodamine B solutions at the wavelength of 556 nm (peak absorption wavelength) against the Rhodamine B concentration in the solution.

RESULTS AND DISCUSSION

Figure 1 illustrates the surface structure of the stainless steel before and after TiO_2 film on it. The uncoated, chemically cleaned steel surface is essentially uniform in structure and has only slight asperities (Fig. 1a). EDX analysis data showed that its elemental composition was close to the expected one: 66.11% iron, 15.78% chromium, 7.19% nickel, 3.35% carbon, and 7.57% oxygen. The TiO_2 films produced on the steel grid surface were of the order of $3\ \mu\text{m}$ in thickness and had a highly porous structure formed by large particles ranging from 80 to 200 nm in size, with particles of the order of 10 nm in size on their surfaces (Fig. 1b). No noticeable structural distinctions between the TiO_2 -coated samples annealed at 450, 500, or 550°C were observed in their SEM images.

Our experiments on Rhodamine B decomposition in an aqueous solution (Fig. 2) showed that the photocatalytic activity of the experimental samples depended on the heat treatment schedule of the sol. In particular, the sample heat-treated at 450°C showed the highest photocatalytic activity, ensuring complete bleaching of the Rhodamine B solution within 80 min of UV irradiation. Raising the heat treatment temperature was observed to reduce both the photocatalytic activity and the amount of the dye adsorbed from the solution during holding of the samples in it.

The surface of the grids used in the photocatalytic experiments was found to have a yellow deposit, which became deeper in color with increasing sol heat treatment temperature. EDX analysis of the composition

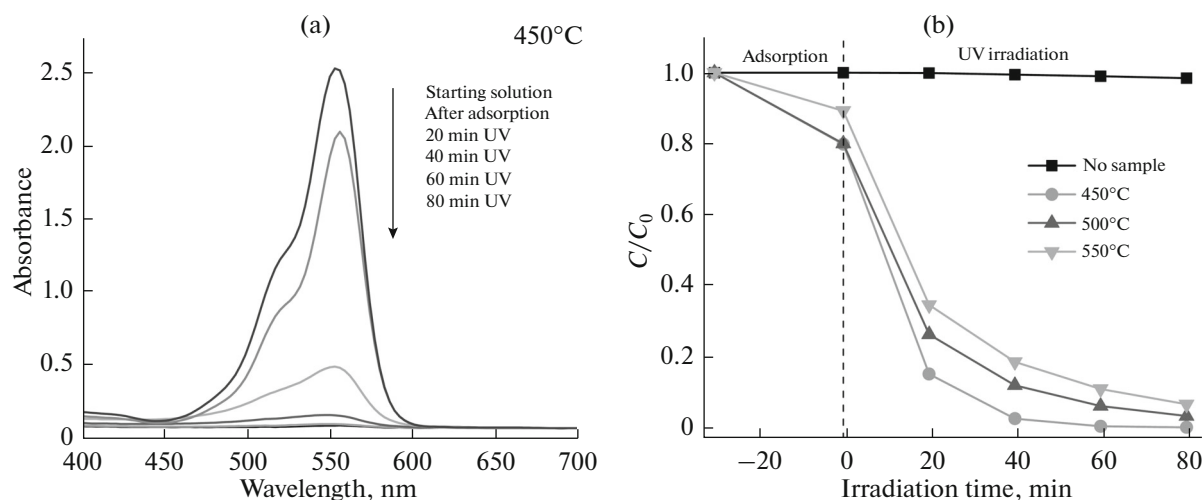


Fig. 2. (a) Absorption spectra and (b) photocatalytic decomposition kinetics of Rhodamine B solutions UV-irradiated in the presence of steel grids with TiO₂ films.

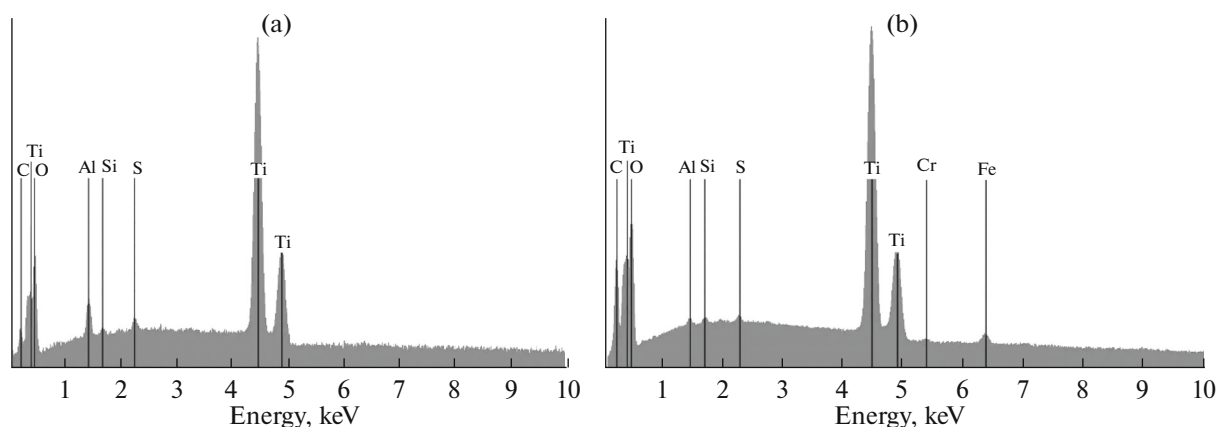


Fig. 3. Energy dispersive X-ray spectra of the surface of TiO₂-coated stainless steel wire after (a) heat treatment at 500°C and (b) subsequent photocatalytic decomposition of Rhodamine B in an aqueous solution for 80 min.

of the TiO₂ film before and after it was used as a photocatalyst (Fig. 3) showed that, in addition to the major components (titanium and oxygen), the surface layer of the as-heat-treated TiO₂ film contained carbon and sulfur, which resulted from the decomposition of the organic compounds and sulfuric acid present in the sol. The observed aluminum and silicon signals arose from the aluminum–silicon sample holder. The absence of signals from the stainless steel components—iron, chromium, and nickel—suggests that the TiO₂ film obtained was opaque to the probing radiation and that none of these components were present on the sample surface. At the same time, after the samples were used in the photocatalytic Rhodamine B decomposition experiments, iron and chromium atoms were detected on their surface (Fig. 3b). No nickel was detected, even though a nickel signal was present in the spectrum of the uncoated stainless steel grid.

To clarify the mechanism responsible for the presence of the stainless steel components, in particular, iron, on the TiO₂ surface, experimental samples were UV-irradiated in distilled water. This treatment also resulted in the formation of a yellow deposit. Etching the samples having a yellow deposit in a 10% hydrochloric acid solution allowed the surface to recover its original, white color. EDX analysis data showed that 10 min of etching reduced the iron content in the surface layer by about a factor of 1.6, bringing it to near the detection limit of this analytical technique.

Assuming that ions of the stainless steel components originated from TiO₂-free zones on the end faces of the steel wires and at the intersections of the wires, we carried out photocatalytic experiments, similar to those described above, in an aqueous Rhodamine B solution and distilled water, using individual wires fully coated with TiO₂. Neither yellow deposit nor iron or chromium was detected on their surfaces.

The experimental data obtained in this study motivated us to conclude that the UV irradiation of a TiO₂ film on a stainless steel substrate that has uncoated regions, with the participation of charge carriers (electrons and holes) generated in the TiO₂, leads to the anodic dissolution of the substrate with the participation of holes and the cathodic deposition of its components onto the film surface with the participation of electrons. The most likely process is then the formation of hydroxides, oxides, or other inorganic compounds of iron and chromium on the TiO₂ surface under irradiation. This leads to a reduction in dye decomposition efficiency because some of the electrons emerging on the surface are consumed in the synthesis of the above-mentioned compounds. A similar result was reported by Butler and Davis [18], who observed a decrease in the photocatalytic activity of TiO₂ under UV irradiation in the presence of Fe³⁺ ions, which was caused by their adsorption on the TiO₂ surface and the formation of iron hydroxides. The deposit reduces the intensity of the UV light reaching the TiO₂ [19], thereby further impeding the formation of •OH radicals, a key reactant in the photocatalytic decomposition of organic compounds, in the aqueous medium near the catalyst surface [20].

The above-mentioned reduction in the photocatalytic activity of experimental samples with increasing TiO₂ film formation temperature in the range 450–550°C can be accounted for by the increase in the percentage of anatase, which is more effective in photocatalytic reactions [21]. In the course of UV irradiation, this leads to a more active deposition of the components of the stainless steel substrate onto the surface of the TiO₂ film, as observed in our experiments, obscuring the photocatalytic properties of TiO₂.

CONCLUSIONS

Uncoated substrate regions have a negative effect on the photocatalytic activity of TiO₂ films on stainless steel substrates and, probably, on other metallic substrates. Under UV irradiation, holes generated in a film stimulate local anodic dissolution of iron and chromium from the substrate in such regions, and electrons emerging on the film surface favor their cathodic deposition, leading to the formation of photocatalytically inactive compounds.

Improving the photocatalytic activity of the film material, for example, by raising the calcination temperature in the sol–gel process, accelerates the formation of the deposit on the film surface, obscuring the photocatalytic properties of the structure on the whole.

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