Anodic TiO_2 nanotube arrays SILAR modified by Ag_xO for visible light photocatalytic applications

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Abstract. To increase the photoactivity of anodic titanium oxide nanotubes in the visible wavelength range, various attempts have been made to increase the absorption spectrum of the material. The heterojunction increases the efficiency of carrier separation and the absorption spectrum of TiO_2 in the visible wavelength range. Ag_xO has attracted considerable attention for the creation of heterojunctions between the TiO_2 layer due to its narrow band gap (1.2 eV), excellent photocatalytic activity and compatibility with TiO_2. In this work, the heterostructures of TiO_2 NTs with deposited Ag_xO by the SILAR method were studied. The morphology and composition of the obtained samples were investigated by scanning electron microscopy and Raman spectroscopy. Photoactivity of obtained samples was investigated under solar simulated light 1.5 AM 40 mW/cm^2.

1. Introduction

Currently, TiO_2 is widely studied and used as a photocatalyst for the decomposition of organic pollutants. However, the TiO_2 band gap is 3.2 eV, which limits the use of TiO_2 in photocatalysis. For photoactivation, TiO_2 requires ultraviolet radiation, which is 4% of the total solar spectrum reaching the surface of the planet [1]. To increase the efficiency of a photocatalyst based on TiO_2, it is necessary to increase the absorption spectrum of the material. Creation of heterostructures by modification of TiO_2 catalyst surface by nanoparticles of semiconductors with smaller band gap than 3 eV can be a promising solution [2, 3]. Silver oxide Ag_2O attracts its attention for making heterojunction with TiO_2 due to its band gap (1.2 eV), good compatibility with TiO_2 [4]. Using a simple and cheap method as SILAR catalyst's heterostructures can be a perspective way to increase photoactivity of TiO_2. However, no data in scientific literature about the effect of the concentration of Ag salt and pH of the solutions on photocatalytic properties of TiO_2 NTs/Ag_2O heterostructures are presented. Thus, the purpose of our work is investigation an influence of Ag precursor concentration and pH solutions used in molecular deposition method from the liquid phase on the photocatalytic characteristics of the material.

2. Experiment

Samples of TiO_2 NTs were obtained by electrochemical oxidation of titanium in ethylene glycol based electrolyte with aded 0.3 wt.% NH_4F and 2 vol.% H_2O. Anodizing was carried out in a thermostated cell at 20° C in two stages. The first stage lasted 30 minutes, after that a formed sacrificial nanotubular layer was removed from the foil surface by cathodic polarization in an 5% H_2SO_4 solution. The second stage lasted 1 h, after which the sample was washed in ethanol and dried in an air stream. After that, the obtained samples were subjected thermal in a muffle furnace at 450 °C for 1 h for crystallization.

In a standard SILAR process, sample of TiO_2 NTs were placed in $AgNO_3$ solution for 5 min to achieve abundant Ag^+ adsorption. After that samples were cleaned by deionized water. The sample was transferred to NaOH solution for another 5 min, and then purified again with deionized water. The following concentrations were used in the work: 0.01, 0.05, 0.1, 0.15, 0.2 M $AgNO_3$ and NaOH (12 - 13,3 pH solutions). Designation of samples: TA-0 (0,1 M without heating), TA-1 (0,01 M), TA-2 (0,05 M), TA-3 (0,1 M), TA-4 (0,15 M), TA-5 (0,2 M), pure TiO_2 NTs. Each sample was modified by 10 SILAR cycles. After that, the samples were annealed in vacuum at 160 °C for 1 hour.

The morphology and composition of the obtained samples were investigated by scanning electron microscopy and Raman spectroscopy. Photoactivity was studied under solar simulated light by photoelectrochemical techniques in 0,1 M Na_2SO_4 solution at 0,5 V vs Ag/AgCl.

3. Results and discussions

SEM images of pure and modified TiO_2 NTs are presented on Figure 1.

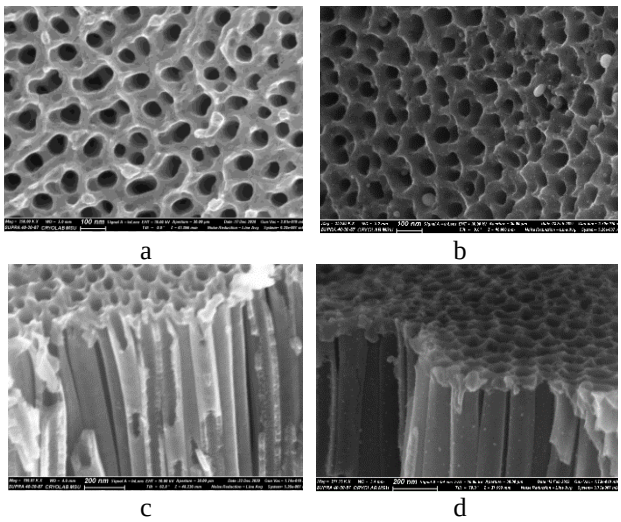

Fig. 1. *SEM images of samples: TiO_2 NTs: top view (a) and side view (c); TA-3: top view (b) and side view (d).*

As can be seen, an obtained Ag_xO NPs in various sizes from 2 nm to ~ 40 nm can be observed. Also, nanoparticles are disposed on walls of TiO_2 NTs arrays. Influence of concentration precursor or pH solution on size distribution of Ag_xO NPs wasn't observed.

Raman shift spectra of obtained TiO_2 NTs samples are presented on Figure 2.

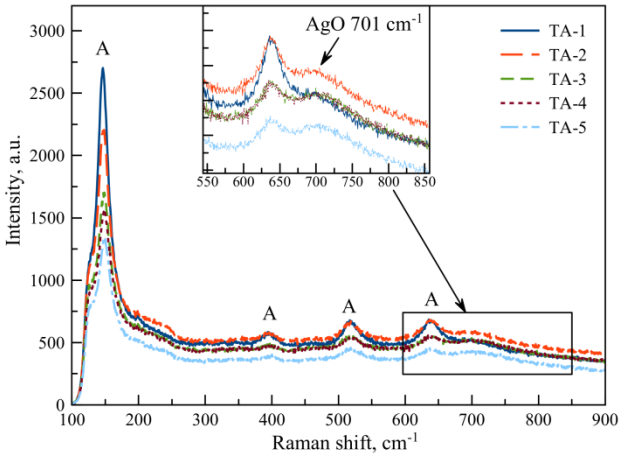

Fig. 2. *Raman spectra of TiO_2 NTs modified AgO_x nanoparticles.*

Peaks (146, 393, 517, 638 cm^{-1}) corresponding to TiO_2 anatase for all samples are observed. As can be seen with increase of concentration of Ag precursor and pH solution a signal intensity from TiO_2 peaks decreases. Also, we detect a wide peak at 701 cm^{-1}, which can be corresponds to AgO [5].

Figure 3 shows photocurrent transients of obtained samples.

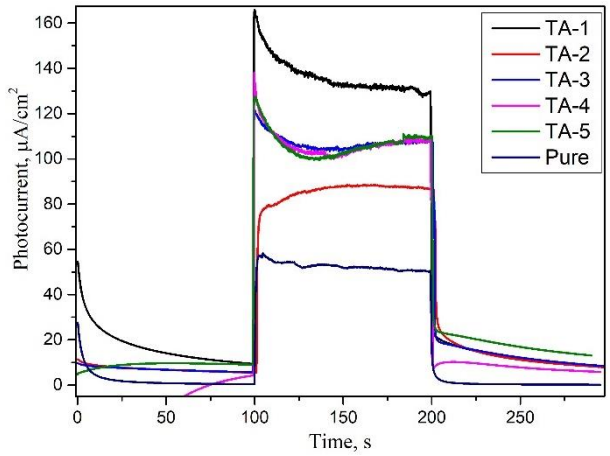

Fig. 3. *Obtained photocurrents of fabricated samples.*

As can be seen, a highest photocurrent attributed for sample TA-1 prepared with 12 pH NaOH solution. An increase of pH and precursor Ag^+ concentration don't lead to next enhance of photoactivity of the material. It should be noted that all variants of methodology lead to increase photoactivity under solar simulated light of the material compared to pure TiO2 NTs sample.

4. Conclusions

Samples of pure TiO_2 NTs and also modified by Ag_xO were obtained. AgO phase was detected by Raman spectroscopy. An influence of Ag+ precursor concentration and pH solutions used in molecular deposition method from the liquid phase on the photocatalytic characteristics of the material was investigated. Can conclude that pH of the solution has most influence on photoactivity of the material. NPs size distribution don't related with concentration of Ag^+ precursor change. Obtained data can be a helpful for planning of photoelectrodes with enhances photoactivity based TiO_2 NTs modified Ag_xO NPs by SILAR method.

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