

Anodic TiO₂ nanotube arrays SILAR modified by Ag_xO for visible light photocatalytic applications

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Abstract

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/cm².

Experimental details

Samples of TiO₂ 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 .

In a standard SILAR process, sample of TiO_2 NTs were placed in AgNO₃ 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 AgNO₃ 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 TiO₂ NTs.



Fig. 1. SEM images of samples: TiO₂ 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 TiO₂ NTs arrays. Influence of concentration precursor or pH solution on size distribution of Ag_xO NPs wasn't observed.

Raman shift spectra of obtained TiO₂ NTs samples are presented on Figure 2.



Fig. 2. Raman spectra of TiO₂ NTs modified Ag_xO 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.

Figure 3 shows photocurrent transients of obtained samples.





Fig. 3. Photocurrent transients of obtained 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.

Figure 4 shows the IPCE spectra for the samples.



Fig. 4. IPCE spectra for pure $TiO_2 NTs$ and $TiO_2 NTs/Ag_xO$

The photoelectric conversion of the samples was carried out by irradiation with visible light with a wavelength of less than 500 nm. The maximum IPCE value (11%) is obtained at 360 nm, and the value at 500 nm is less than 1%. It can be concluded that the TA-1 sample has the maximum efficiency at the ratio of the electron yield to the number of incoming photons.

Conclusions

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 TiO₂ NTs modified Ag_xO NPs by SILAR method.