EFFECT OF THE CU IONS IMPREGNATION CONDITIONS ON THE ANODIC TiO_2 PROPERTIES

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Anodic titanium oxide (TiO_2) as biocompatible, non-toxic material having a good chemical stability is often used in photocatalysis, photoelectrochemical water splitting, and medicine [1-3]. However, its high band gap (3.2 eV) limits its applications

as catalysts and causes that only UV light can be absorbed [4]. Among different approaches that can be used to reduce the band gap, a wet impregnation method seems to be an easy and effective strategy to obtain enhanced materials properties. Therefore, in this work, studies on the influence of copper ion concentration on properties of anodic TiO_2 samples impregnated with copper (II) acetate solutions were presented.

1. Experimental

Anodic titanium oxide was fabricated by a three-step anodization in an ethylene glycol-based electrolyte containing 0.38% wt. NH_4F and 1.79% wt. H_2O at a constant potential of 40 V.

The samples of nanoporous titanium oxide layers were modified using the impregnation method with $Cu(CH_3COO)_2$ solutions at various concentrations (10 – 50 mM). The samples were immersed in the solution containing the appropriate concentration of transition metal ions for 10 minutes and then dried at 80 °C for 20 min. This cycle was repeated 5 times. The obtained samples were then annealed at 400 °C for 2h.

The morphology and chemical composition of synthesized materials were investigated by field emission scanning electron microscopy (FE-SEM/EDS).

The photoelectrochemical measurements were carried out using a potentiostat in a three-electrode Teflon cell, where the tested sample was used as a working

electrode, the platinum wire as a counter electrode, and the silver chloride electrode was a reference electrode. The photocurrent vs. time curves were recorded in a 0.1 M KNO_3 aqueous solution under the applied potential of 1 V vs. Ag/AgCl. A pulse illumination in the range of 300 – 600 nm with a 2 nm wavelength step and 10 s light and 10 s dark cycles were used.

2. Results and discussion

In order to determine a surface distribution of copper and its content, elemental EDS mapping was carried out. As can be seen from Fig. 1, the synthesized materials possess a porous morphology comparable with the anodic TiO_2. The EDS map demonstrated that copper is uniformly distributed over the surface of anodic TiO_2, and the average Cu content (marked with red) in anodic samples decreases with increasing copper ion concentration in the impregnating solution.

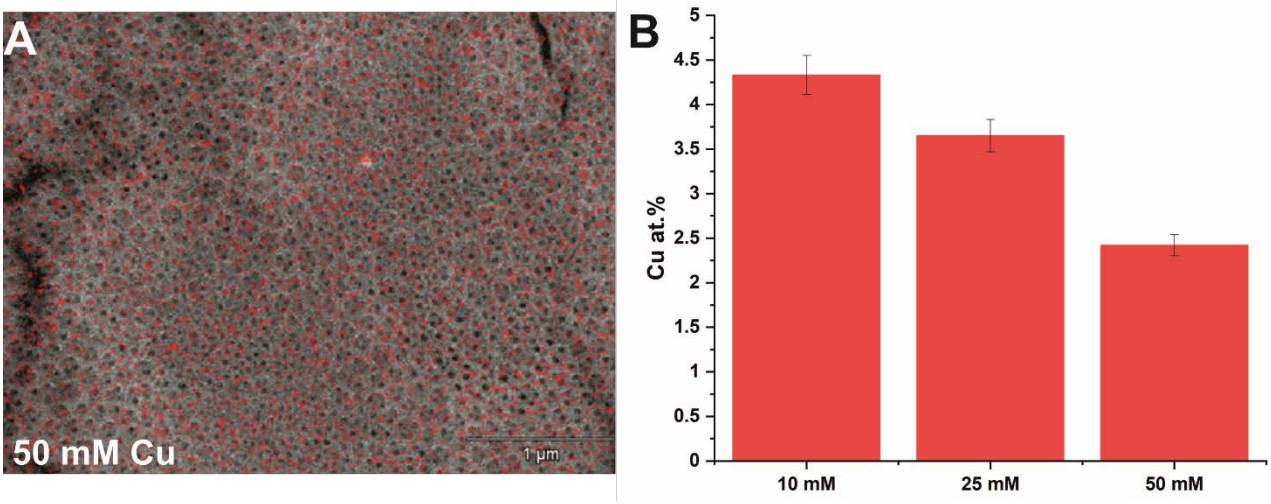

Fig.1. (A) FE-SEM/EDS map of anodic TiO_2 impregnated in 50 mM $Cu(CH_3COO)_2$ and annealed at 400 °C for 2 h. (B) Average copper content in the samples impregnated in solutions with different concentrations of $Cu(CH_3COO)_2$.

To investigate the influence of concentration of $Cu(CH_3COO)_2$ in impregnation solution on the photoresponse of synthesized samples, the photoelectrochemical measurements were performed. For non-modified anodic TiO_2 layers maximum photocurrent density values were typically observed at 354 nm. However, for modified TiO_2 samples the maximum of generated photocurrent was slightly shifted towards he visible light region. Values of band gap energies, which are shown in Fig. 2, are lower than for the TiO_2 samples impregnated in distilled water.

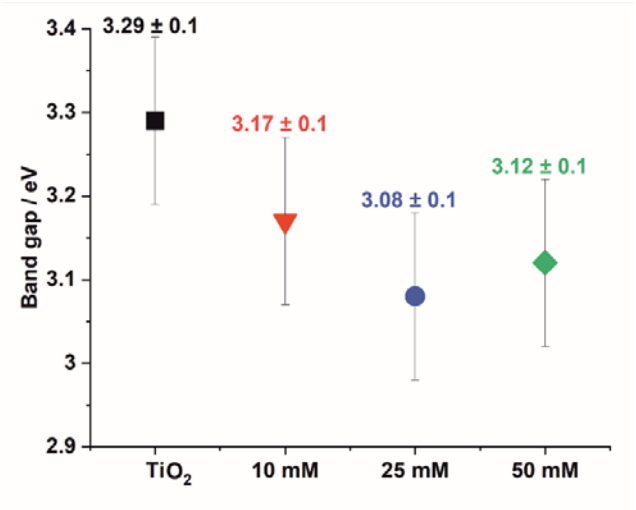

Fig. 2. Band gap values estimated from photoelectrochemical measurements.

3. Conclusion

The studies showed that the structure of anodic TiO_2 samples impregnated with Cu ions was changed and depend on the concentration of transition metal ions used. The modified TiO_2 materials exhibited different photoelectrochemical response from those observed for unmodified TiO_2 layers. The band gap energy values for the modified samples, which were determined by photoelectrochemical measurements, are slightly lower when compared with the non-modified.

It should be mentioned, that proposed modified anodic TiO_2 samples can be promising materials working under solar illumination. However, further research is needed to fully understand the influence of impregnation conditions on semiconducting properties of anodic TiO_2 layers.

References

[1] U. Diebold, The surface science of titanium dioxide, Surf. Sci. Rep. 48 (2003) 53–229.

[2] K. Nakata, A. Fujishima, TiO_2 photocatalysis: design and applications, J. Photoch. Photobio. C 13 (2012) 169–189.

[3] R. Aguirre Ocampo, F. Echeverría Echeverría, Effect of the anodization parameters on TiO_2 nanotubes characteristics produced in aqueous electrolytes with CMC, Appl. Surf. Sci. 469 (2019) 994–1006.

[4] A. Ghicov, P. Schmuki, Self-ordering electrochemistry: a review on growth and functionality of TiO_2 nanotubes and other self-aligned MO_x structures, Chem. Commun. (2009) 2791–2808.