Fabrication of TiO_2-Ru(O_2)/Al_2O_3 Composite Nanostructures on Glass by Al Anodization and Electrodeposition

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Materials in the TiO_2-RuO_2 system are of considerable interest for many applications such as industrial electrochemistry, electro- and photo-catalysis, solar cells, electronics, chemical sensors, and energy storage systems.[1-3] Many works have been done to synthesize various TiO_2-RuO_2 materials in form of aerogels,[1] powders,[2] and coatings[3] through sol-gel method[1, 2] and electrodeposition.[3] Our approach aims at exploring a novel process to fabricate TiO_2-RuO_2 nanowire or nanotube arrays on glass substrates to improve or enhance the properties of TiO_2-RuO_2 materials for many potential applications.

In our previous works,[4-6] we had described the fabrication and characteristic of arrayed oxide (e.g., TiO_2) nanotubules and metal (e.g., Ni) nanowires on glass by combining Al anodization with a sol-gel process or with a *dc* electrodeposition. In the present study, we report a novel process to electrosynthesize titanium oxide-ruthenium nanowire arrays on glass by a cathodic electrodeposition in porous alumina nanostructures.

A highly pure aluminum layer (99.99%, 1.5~2 μm), which was sputter-deposited on a glass substrate (25 × 110 × 1.1 mm) with a tin-doped indium oxide (ITO) film, was used as the starting specimen. The specimens were first anodized potentiostatically in phosphoric, oxalic, or sulfuric acid solutions to obtain porous alumina films with different pore densities and dimensions, and then immersed in a phosphoric acid solution to remove the insulative barrier layer of the anodic alumina films. The porous alumina structures on ITO/glass were used as template electrodes in electrodeposition. The electrolyte for electrosynthesis was a mixed ethanol-water solution containing titanium chloride ($TiCl_3$), ruthenium chloride ($RuCl_3.nH_2O$), and peroxide (H_2O_2, 30% in water). Cathodic electrosynthesis was continuously carried out in a constant current mode till the deposits filled the pores completely. Finally, the specimens were heated at 873 K for 2 h to fulfill the crystallization of titanium oxide and the oxidation of ruthenium. The morphology of the surface and the fracture sections of the specimens were observed by FESEM with EDXA. The crystallographic structures of electrodeposited specimens were analyzed by XRD and TEM. The transmittance spectra of the specimens were measured by a UV-vis spectrometer.

Porous alumina films with parallel channels and ϕ4~120 nm in diameters can be achieved through the anodization of sputtered Al layers on ITO/glass substrates. The anodic alumina nanostructures possess characteristic barrier layers that are much thinner than the pore walls. This enables the barrier layers to be removed by a chemical dissolution while still preserving the porous structures on substrates. Through a cathodic electro-deposition, titanium and ruthenium ions and/or their complex ions are reduced into metals and/or hydroxides in the nanopores of alumina films on ITO/glass, forming a composite nanostructure as shown in **Figure 1.** The electrodeposits fill in the pores of anodic alumina films uniformly and densely. The EDAX results show that the electrodeposits composed of Ti, Ru, and O elements. According to XPS analysis, titanium is identified to be the oxide, and ruthenium to be in its metallic state.

Figure 2 shows the UV-Vis transmittance spectra of various nanostructures on ITO/glass substrate after anodization, electrodeposition, and calcinations. The average transmittance of the anodized specimen is close to that of the ITO/glass substrate, due to the complete anodization of aluminum layer and the transparency of anodic alumina. After electrodeposition, the transmittance of the specimens decreases greatly due to the filling of the TiO_2-Ru in the pores of alumina film. After heated at 837 K for 2h, the color of the electrodeposits changes from grey to milky, and the specimens' transmittance increases apparently, inferring the oxidation of ruthenium and/or the crystallization of titanium oxide.

References

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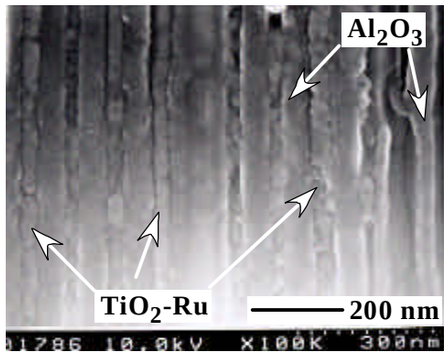

Fig.1 FESEM images of TiO_2-Ru/Al_2O_3 Composite Nanostructures on ITO/glass substrate.

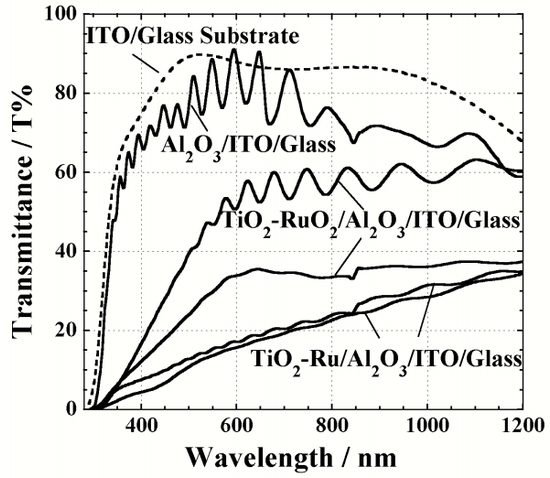

Fig.2 UV-vis transmittance spectra of various composite nanostructures on ITO/glass substrate.