



In-situ electrochemical doping of nanoporous anodic aluminum oxide with indigo carmine organic dye



Wojciech J. Stępniewski^{a,*}, Małgorzata Norek^a, Bogusław Budner^b, Marta Michalska-Domańska^{a,b}, Agata Nowak-Stępniewska^b, Aneta Bombalska^b, Miron Kaliszewski^b, Anna Mostek^a, Sanjay Thorat^{c,1}, Marco Salerno^c, Michael Giersig^d, Zbigniew Bojar^a

^a Department of Advanced Materials and Technology, Faculty of Advanced Technology and Chemistry, Military University of Technology, 2 Kaliskiego Str., 00-908 Warszawa, Poland

^b Institute of Optoelectronics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warszawa, Poland

^c Department of Nanophysics, Istituto Italiano di Tecnologia, via Morego 30, Genova I-16163, Italy

^d Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

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ABSTRACT

Nanoporous anodic aluminum oxide was formed in sulfuric acid with addition of indigo carmine. During anodizing, the organic dye was incorporated into the porous oxide walls. X-ray photoelectron spectroscopy revealed the presence of nitrogen and sulfur in the anodic aluminum oxide. Two types of incorporated sulfur were found: belonging to the sulfate anions SO_4^{2-} of the electrolyte and belonging to the C-SO_3^- side groups of the indigo carmine. Raman spectroscopy confirmed the incorporation and showed that the inorganic–organic hybrid material inherited optical properties from the indigo carmine. Typical modes from pyrrolidone rings, unique for indigo carmine in the investigated system (650 and 1585 cm^{-1}), were found to be the strongest for the greatest anodizing voltages used. Despite the indigo carmine incorporation, the morphology of the oxide is still nanoporous and its geometry is still tuned by the voltage applied during aluminum anodization. This work presents an inexpensive and facile approach to doping an inorganic oxide material with organic compounds.

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1. Introduction

Self-organized nanoporous metal oxides attract attention of the researchers due to their numerous applications. Since the time when Masuda and Fukuda reported about the fabrication of self-organized nanoporous anodic aluminum oxide two decades ago [1], numerous metals have been successfully anodized to form nanoporous or nanotubular morphology. It is a well-known fact that during the growth of anodic oxide, hydroxyl groups (OH^-) are generated in the electrolyte and are attracted by the anode [2]. Moreover, even electrolyte anions like sulfates, oxalates, or phosphates are being attracted and adsorbed on the anode surface, and next are being incorporated into the growing oxide [3]. This phenomenon was studied by Le Coz et al. for anodic aluminum oxide (AAO) formed in phosphoric acid⁴. It was found that the majority of the phosphate anions are incorporated in the outer part of AAO. Le Coz et al. recently reported that they found up to ~2.7 at.% of phosphorous in AAO [4–5]. Berger et al. reported even up to 4.45 at.% of fluoride in anodic titania as a result of F^- anions incorporation during

anodic oxide growth in ethylene glycol electrolyte of HF [6]. The phenomenon of anions incorporation was originally reported by the researchers as a form of contamination of the nanoporous oxide, disadvantageous not only in terms of chemical composition, for example, affecting the optical properties of the resulting material [7], but also for its consequences on pores arrangement during the self-assembly growth. However, while this effect is quite difficult to limit, researchers started to turn it into a positive effect, namely, a chance for directed and functional doping of the porous oxide nanostructure. Thus, the incorporation effect was put to work and allowed to dope e.g. anodic TiO_2 with N [8] and Ru [9–10], Ta_2O_5 with N [11], or WO_3 with N [12]. This anodic oxide doping brought contribution in catalysis [9–10], photovoltaics [8], and water splitting [12]. However, expanding the field of the doping of anodic oxides is still demanded due to the further possible nanotechnological applications.

Moreover, also industrial companies try to develop technologies based on the organic compounds incorporation into the anodic aluminum oxide [13–14]. For the industry-oriented researchers, the incorporation of organic compounds into AAO is a key for the adhesion enhancement [13–14].

In this paper, we report for the first time on the fabrication of nanoporous AAO doped in-situ with the organic dye indigo carmine (IC). The dye was added to the electrolyte prior to the anodization,

* Corresponding author.

E-mail address: wojciech.stepniowski@wat.edu.pl (W.J. Stępniewski).

¹ Currently at: Department of Physics, Laboratory of Nanoscience, University of Trento, via Sommarive 13, I-38,123 Trento, Italy.

and due to the incorporation phenomenon, it doped the formed oxide, as confirmed and characterized in this study. High chemical stability of IC and its conjugated π electrons make this dye interesting as a dopant in anodic oxides [15].

The main aim of the research was to investigate the phenomenon of the indigo carmine incorporation into anodic aluminum oxide and to examine whether the anodic oxides will gain the optical properties from the incorporated dye.

2. Experimental

2.1. UV–Vis spectroscopy

UV–Vis spectra of IC solutions were taken with UV–Vis Cary spectrophotometer (Varian, Perkin-Elmer, MA, USA) at wavelength range from 200 to 750 nm with wavelength resolution of 1 nm. 5×10^{-4} M IC solution was prepared in de-ionized (DI) water and in 20 wt.% H_2SO_4 to study the stability of the dye in the electrolyte used further in anodizations.

2.2. Dynamic light scattering

Dynamic light scattering (DLS) measurements were carried out on a Zetasizer ZS-Nano system (Malvern Instruments Ltd., UK), using disposable polymethyl-methacrylate cuvettes. Typically, both values of size and Zeta-potential of the colloidal particles resulted from 5 measurements of 4 runs each. The resulting values are expressed as mean \pm standard deviation, ($N = 5$). To assess the stability of the results, the experiments were repeated after different times since dispersion of IC in the respective solvent (DI water only or aqueous solution of the acid used for aluminum anodization), namely, soon after dispersion, after 1 h, 5 h, and 1 day. For both solvents, no significant effect of the different measurement times was detected. For the size measurements, the mean is taken from the distribution by number of the suspended particles.

2.3. Fabrication of AAO

Two-step self-organized anodization of 99.9995% purity aluminum (Puratronic, Alfa Aesar) was conducted in 20% wt. H_2SO_4 with addition of 5×10^{-4} M of ultrapure (pro analysis) IC (POCh, Poland). After 1 h long anodization, the formed poorly organized oxide was removed with chemical etching (6 wt.% H_3PO_4 and 1.8 wt.% H_2CrO_4 at 60 °C for 90 min). Next, the samples were re-anodized at the same set of operating conditions for 1 h. Anodizations were performed at two different temperatures: 0 and 15 °C. 0 °C anodizations were performed at voltages ranging from 15 to 25 V, while 15 °C anodizations were performed at voltages from 15 to 19 V, as above 19 V electrochemical field-assisted dissolution of the aluminum occurred instead of anodization with growth of oxide overlayer.

2.4. Imaging of AAO

FE-SEM imaging was performed with a high-resolution field emission scanning electron microscope Quanta 3D FEG (FEI, USA) in low vacuum mode dedicated to non-conductive samples. Quantitative image analyses were carried out with NIS-Elements software (Nikon, Japan) and WSxM software [16–17] (Nanotec Electrónica, Spain).

2.5. Chemical analysis of doped AAO

Surface chemical composition analyses were performed by X-ray photoelectron spectroscopy with R3000 analyzer (Scienta, Sweden) and X-ray lamp with the Mg K α cathode with photons energy of 1253 eV (Prevac, Poland).

2.6. Spectroscopy of doped AAO

The characterization of solid products was performed with Raman spectroscopy using inVia Raman Microscope (Renishaw, UK) with 633 nm excitation.

The photoluminescence spectra were taken with FL 900 spectrofluorometer (Edinburgh Instruments) with Xe lamp, using front-surface measurement mode. The excitation wavelength was 600 nm and emission spectra were recorded from 620 to 750 nm.

3. Results and discussion

First of all, for the dopant to be effective, its stability in the acidic electrolyte used for fabrication of AAO (20% wt. H_2SO_4) had to be assessed. UV–Vis absorption spectra were acquired after 1 h since dispersion of IC in the electrolyte, and then again on the subsequent day, after overnight incubation. The absence of significant changes in the spectra, as apparent in Fig. 1a, shows that IC is stable in the chosen electrolyte. However, Zeta-potential measurements of the solution including the dye, carried out by DLS after similar times since dispersion as for the absorption spectra, show that at acidic pH protonation of the IC anions occurs. Stability over the time is provided by the absolute value of the Zeta-potential staying always above the threshold value of ~ 25 mV, even though it underwent a reversal sign from negative to positive (from -27 ± 8 to $+36 \pm 4$ mV) after mixing with the aqueous

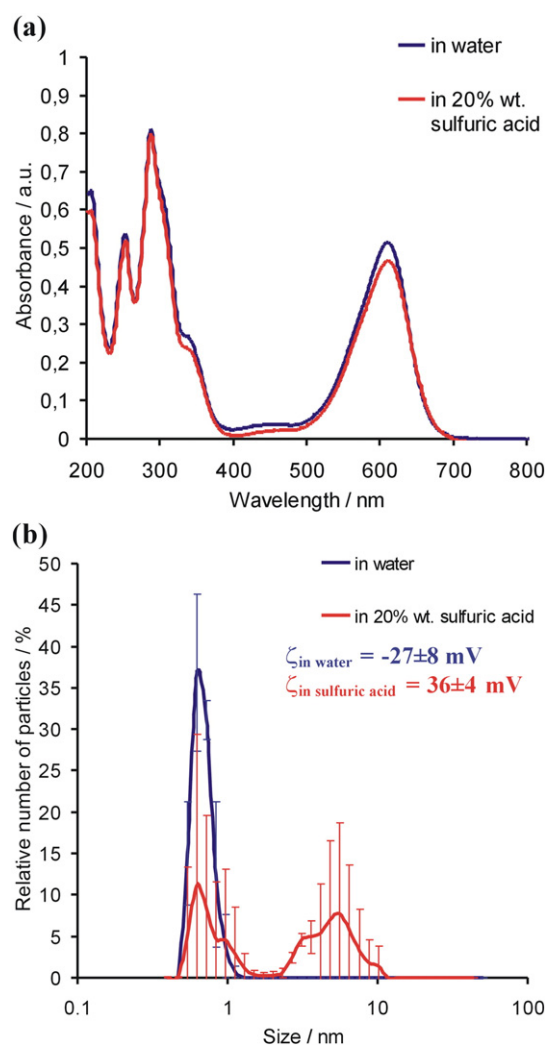


Fig. 1. UV–Vis absorption spectrum (a) and DLS particle size distribution of IC dissolved in DI water and in 20 wt.% H_2SO_4 .

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