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# Synthesis of copper and zinc oxides nanostructures by brass anodization in alkaline media

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## ABSTRACT

Copper and zinc oxides are routinely used in the manufacture of electronic devices due to their favorable band gap energies. In this work, synthesis of copper and zinc oxides by anodization of brass foil was performed in alkaline aqueous solution at room temperature. The range of independent anodization parameters investigated was as follows: sodium hydroxide (NaOH) and potassium hydroxide (KOH) concentration (0.05–0.3 M/L), anodizing time (15–120 min) and voltage (3–24 V). Effects of additives such as ammonium chloride, ammonium fluoride and ammonium sulfate were investigated. Structural properties of the oxides film were studied with field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Anodizing of the brass foil in alkaline media resulted in the formation of copper and zinc oxide nanostructures (CuO, ZnO) with dimensions up to 100 nm. The nanostructures of both oxides were obtained in electrolytes containing 0.1 M NaOH at 12 V for 60 min and 0.2 M KOH at 6 V and for 60 min. Diverse morphologies were observed such as spherical, flower-like, porous, flake-like, pyramidal, polygonal and cubic in nano, submicron and micron scales in different conditions.

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## 1. Introduction

Anodization technique has been employed for a long time to ornament a metal surface or to increase corrosion/wear resistance [1]. This method is a very cost-effective method to produce uniform and adhesive oxide films on metals [2] and is a surface treatment process that has been successfully used to grow a variety of nanostructures on many metal surfaces, with the resulting films successfully used in different applications [3].

Metal oxides exhibit a wide range of properties depending on bonding between the metal ion and oxygen and their crystal structure. Therefore, these oxides have become one of the most attractive materials in applications such as light emitting diodes, field effect transistors and solar cells [4].

Copper oxide is a p-type semiconductor with a band gap around 2 eV that has recently stimulated interest because of its potential applications in random access memories [5], low-cost solar cells [6] and gas sensors [7] among other devices. Zinc oxide is a well-known semiconducting and piezoelectric material. Its wide direct band gap energy of 3.37 eV with a large excitation binding energy of 60 meV at room temperature is much larger than those of other semiconductor materials [8].

Due to its unique properties, zinc oxide nanomaterials have been considered to have great potential applications in ultraviolet lasers, solar cells, gas sensors, bio-detectors, UV light-emitting diodes, photo catalysts, field emitter, transparent conductors, etc. [9]. Copper and zinc oxides are also used routinely in the manufacture of electronic devices due to their favorable band gap energies, potential low production cost, non-toxic nature and abundance of raw material. As a consequence, the physical properties of thin films of these oxides continue to be studied [10].

Previous studies paid more attention to the fabrication of these two oxides together with different costly or time consuming methods such as vapor deposition (CVD and PVD) [4,11,12] spray pyrolysis [13–15], spin coating [16,17] and electrodeposition [6]. Although there is no previous study on the preparation and characterization of these two oxides simultaneously, by anodization, there are several researches that have studied the synthesis of copper oxide [3,18,19] and zinc oxide [2,9] separately, by anodization. However, presence of these elements in the oxide lattice, Zn in copper oxide or Cu in zinc oxide lattice can improve its optical and electrical properties like band gap condition [14–16]. Also gas-sensing properties of the oxides can be improved [20,21]. For instance, selectivity of ZnO gas sensors can be increased with doping Cu in the ZnO lattice by interstitial diffusing.

This study provides a simple and rapid method for synthesizing different copper and zinc oxide nanostructures on the surface of brass, simultaneously. In this work, we anodized brass foil in order to investigate the effect of electrochemical parameters on its oxidizing process and study the mechanism of copper and zinc oxide formation on the

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**Table 1**  
Tested conditions for anodization of the brass foil.

| Selected electrolyte                   | Parameter                     | Values       |
|--|-------------------------------|--------------|
| NaOH                                   | Voltage (V)                   | 6–12–24      |
|  | Electrolyte concentration (M) | 0.05–0.1–0.2 |
|  | Anodizing time (min)          | 15–30–60     |
| KOH                                    | Voltage (V)                   | 6–12         |
|  | Electrolyte concentration (M) | 0.1–0.2      |
|  | Anodizing time (min)          | 60           |
| NaOH + NH <sub>4</sub> Cl              | Voltage (V)                   | 12           |
|  | Additive concentration (M)    | 0.025–0.05   |
|  | Anodizing time (min)          | 30–60        |
| NaOH + NH <sub>4</sub> F               | Voltage (V)                   | 12           |
|  | Additive concentration (M)    | 0.025        |
|  | Anodizing time (min)          | 30           |
| NaOH + NH <sub>4</sub> SO <sub>4</sub> | Voltage (V)                   | 12           |
|  | Additive concentration (M)    | 0.025        |
|  | Anodizing time (min)          | 30           |

brass. It is worth mentioning that some preliminary tests with both NaOH and KOH were done and it was found that sodium hydroxide (NaOH) medium leads to a proper surface in terms of adhesion, homogeneity and nano-structure of the texture. Also, effect of three different additives ammonium chloride (NH<sub>4</sub>Cl), ammonium fluoride (NH<sub>4</sub>F) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) was studied.

## 2. Experimental procedure

Pure commercial brass foil with thickness of 0.4 mm was purchased from Bahonar-e-Kerman Company. The EDS of the non-anodized brass resulted in 64.45% Cu and 35.54% Zn. Spark Emission Spectroscopy (SES) analysis of the sample confirmed the above-mentioned composition. Prior to anodization, samples were mechanically polished with a grinding paper to remove the native oxide followed by a deionized water rinse. It was degreased in acetone and ethanol for 10 min of ultrasonic cleaning bath (BANDELIN sonorex, 30 W), washed with deionized water. Brass foil sample sizes were 6 × 2.6 cm<sup>2</sup> with 2.8 × 2.6 cm<sup>2</sup> immersed in the electrolyte. The anodization was conducted in a two-electrode cell with brass foil as the working electrode and stainless steel foil as the counter electrode. The distance between the two electrodes was 50 mm, under constant applied voltage at room temperature (approximately 25 °C). At high voltages or longer time a cooling bath was used to remain the temperature constant. The specimens were anodized at different conditions, which is shown in Table 1. The NaOH and KOH electrolytes at concentrations from 0.05 M to 0.2 M in pH ranges 12–14 were used. Effect of three different additives was studied; ammonium chloride, ammonium fluoride and ammonium sulfate. After performing some tests, among these additives NH<sub>4</sub>Cl revealed better results and subsequently three extra tests were done at different concentrations of this additive. Different potentials from 3 to 24 V and anodizing time ranging from 15 to 60 min were applied. During the anodization, the stirring speed was kept constant.

Finally, the thin film was grown on the brass foil and thoroughly washed with deionized water to eliminate residues and dried in air at room temperature. The morphology and composition of the films

were characterized by a field emission scanning electron microscope (FESEM) (Hitachi s4160, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS-CamScan MV2300) analysis, operated at an accelerating voltage of 15 kV. To prevent the penetration of primary electrons into the substrate, all samples were tilted 20 to 30° for EDS analysis. Thus, the detected X-rays were more likely to be emitted from the surface. The formed phases were identified by X-ray diffraction (XRD-X'pert Philips with Cu Kα radiation). Before FESEM measurements, the samples were first coated with a Pt layer with thickness of 3 nm by a sputter coater (bio rad, e5200, Japan).

## 3. Results and discussions

### 3.1. Anodization in NaOH aqueous electrolyte

#### 3.1.1. Effects of voltage

In order to examine effects of the applied voltage on the morphology and composition of the film three conditions of 6, 12 and 24 V were selected for 60 min anodization in 0.1 M NaOH. Table 2 shows atomic percentages in the anodized films determined by EDS analysis.

According to Table 2(a, b, c), increasing the applied voltage from 6 to 12 V, atomic percentage of oxygen remained almost constant at ca. 38% and further increasing of the voltage to 24 V resulted in a dramatic increase in atomic percentage of oxygen. This is an indication of the presence of metal oxide on the surface of the film. During brass oxidation and based on the reduction potentials in this electrochemical system zinc has higher tendency to oxidizing than copper [22]. Therefore, during brass anodization zinc oxide is formed first, followed by copper oxide.

Fig. 1 shows Pourbaix diagrams for copper and zinc in aqueous electrolytes. From the thermodynamic viewpoint Pourbaix diagrams predict possible stable species at specific potential ( $E_{SHE}$ ) and pH [23]. As seen in Fig. 1, at the conditions used for Cu–H<sub>2</sub>O–NaOH and Zn–H<sub>2</sub>O–NaOH systems, CuO and ZnO are the predominant species of copper and zinc present in the system. Therefore, it can be predicted that the metal oxide species on the surface of brass is most probably CuO and ZnO.

Fig. 2(a) shows the FESEM image of a brass surface anodized at 6 V. As shown, spherical particles were formed with an average diameter of ca. 50 nm (10<sup>−9</sup> m). Fig. 2(b, c) illustrates flowerlike nanostructures prepared at 12 V and 24 V, respectively. As it can be seen in Fig. 2(b) each flower has a dimension of 100 nm and is composed of some sheet-like nanopetals. The thickness of the nanopetal is ca. 30 nm on average. Considering only the FESEM images, voltages of 12 V and 24 V seem to be appropriate, but from both EDS and FESEM results and considering our main objective of reaching to a nanostructure, fully oxide layer which contains both copper and zinc oxides, it can be concluded that the voltage of 12 V at 60 min anodizing time in 0.1 M NaOH illustrated a better result.

#### 3.1.2. Effects of NaOH concentration

To investigate the effects of electrolyte concentration, the NaOH concentration was changed (0.05, 0.1 and 0.2 M) while all other parameters were kept the same at 12 V and 60 min. At NaOH concentrations of 0.05 and 0.1 M copper and zinc oxides were prepared. As it can be seen in Table 2(b, d), the atomic percentage of oxygen increased with the

**Table 2**  
EDS analysis results of the films prepared by anodization in NaOH.

| Sample | Anodizing conditions      |        |         | Cu (at.%) | Zn (at.%) | O (at.%) |
|--------|---------------------------|--------|---------|-----------|-----------|----------|
|        | Electrolyte concentration | Time   | Voltage |           |           |          |
| A      | 0.1 M                     | 60 min | 6 V     | 38.0      | 24.8      | 37.2     |
| B      | 0.1 M                     | 60 min | 12 V    | 36.9      | 23.1      | 39.9     |
| C      | 0.1 M                     | 60 min | 24 V    | 26.0      | 18.7      | 55.7     |
| D      | 0.05 M                    | 60 min | 12 V    | 44.4      | 24.9      | 30.7     |
| E      | 0.1 M                     | 15 min | 12 V    | 45.5      | 32.1      | 20.8     |
| F      | 0.1 M                     | 30 min | 12 V    | 40.2      | 30.3      | 29.5     |

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