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PROPERTIES OF Cu/Zn OXIDE NANOSTRUCTURES FORMED BY PLASMA-ACTIVATED ELECTROLYSIS

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Abstract. In this work, the low-temperature plasma-activated electrolysis method has been developed and implemented for the synthesis of metal oxide (CuO, ZnO) nanoparticles (NPs) and oxide-based composite thin films.

1. INTRODUCTION

The development of novel composite nanomaterials has recently significantly contributed to the advances reached in the fields of electrochemical sensors and biosensors. The efficiency of the sensors produced is determined by several major parameters, including composition, structure and morphology of the constituent nanoparticles (NPs) and their surface. All these parameters are largely determined by the synthesis conditions of nanocomposites. Among the different techniques for NPs synthesis, plasma assisted processes in liquids have received much attention last years due to the combination of such advantages, as high production rate, versatility with the possibility of control over the NPs formation process. In this work, the low-temperature plasma-activated electrolysis method has been developed and implemented for the synthesis of metal oxide (CuO, ZnO) nanoparticles (NPs) and oxide-based composite thin films. A simultaneous anodic dissolution of the metal foils served as solid precursors was discovered followed by further assembly of the formed metal components into nanoparticles under reactions with plasma-produced species. As a result, the developed method does not require addition of any

toxic precursors and therefore benefits from the absence of further purification steps. Moreover, no additional annealing is required as compared to the existing methods. The further modification of the method has been demonstrated for simultaneous assembly of the synthesized oxides nanoparticles from colloidal solution on a substrate that emphasizes the versatility of the developed approach.

2. EXPERIMENTAL

The scheme of the experimental setup developed for the formation of composite nanoparticles both in colloid and as thin films are presented in Figure 1a. In the proposed approach, NPs formation occurs in result of dissolution of solid combined anode, composed of Cu and Zn foils, after high voltage application (1.5-3 kV) between the combined anode and a hollow capillary cathode with Ar flowing through it. For their dissolution, the anodes are submerged into the distilled water used as a solvent. The argon flow rate was about 20 mL/min. The cathode was made of stainless steel, its outer diameter is 800 μm, and the inner diameter is 500 μm and is located at a distance of 3-8 mm from the liquid surface. The advantage of this approach is that it operates under normal atmospheric conditions and does not require a sealed chamber. As the power source voltage increased, a breakdown of the discharge gap between the liquid surface and the end of the opposite electrode occurred, and a glow discharge of atmospheric pressure was ignited. The magnitude and stability of the discharge current characteristics depended on the source voltage and the argon pumping rate.

To assembly the growing nanomaterial into thin-film structures, an additional substrate was placed in the cuvette, which was a copper plate or carbon cloth. This substrate was connected to the power source through an additional ballast resistance (6.8 MΩ). The composition, morphology, and optical properties of the resulting nanoparticles and films have been studied in dependence on the experimental conditions. The morphology and structure of the formed NPs were evaluated using scanning electron microscopy (SEM) technique with a SEM microscope SUPRA 55WDS (Carl Zeiss, Germany). Additional information on the phase composition, crystal and defect structure of the prepared NPs was obtained from the results of X-ray diffraction (XRD) and Raman spectroscopy. For Raman spectroscopy, the colloidal solution was deposited onto an aluminum foil and dried at 80 °C to remove excess of water. Raman spectra were registered in the range of 100–1000 cm^{-1} using a scanning probe confocal microscope\spectrometer NanoFlex (Solar LS, Belarus) with a laser excitation source at 470 nm.

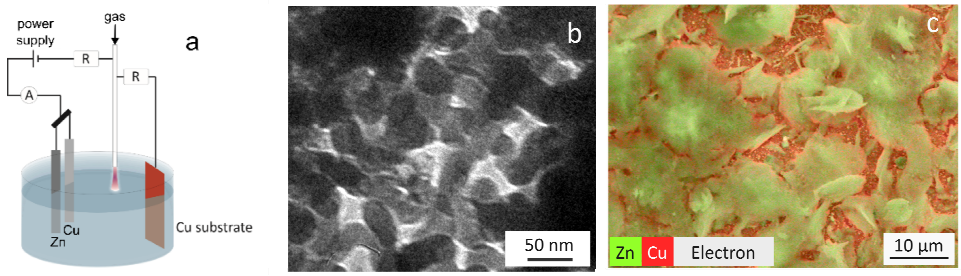

Figure 1. Plasma activated electrolysis synthesis and properties of Cu/Zn oxides nanostructures: a – scheme of the experimental setup, b –TEM and c - SEM image of the NPs deposited on the copper substrate with EDX mapping of Cu and Zn

3. RESULTS AND DISCUSSION

The morphology of the prepared Cu/Zn nanoparticles was investigated by transmission (TEM) and scanning (SEM) electron microscopies (Fig. 1 b,c). The TEM results indicate that plasma-assisted synthesis results in the production of elongated elliptically shaped nanoparticles that however are prone to agglomeration into the elongated branched structures depicted in more details in Figure 1c (SEM image). The elemental maps performed to find the distribution of the constituent elements in the prepared samples, were acquired using the EDX technique coupled with SEM. The results of the EDX mapping showed that the prepared nanoparticles mainly consist of copper, zinc and oxygen with Cu:Zn atomic ratio close to 1:1. This result is indicative of Cu, Zn and O being bound in a composite as will be further proved by XRD and Raman techniques.

Additional information about the crystal and defect structure of the prepared nanomaterial was obtained from Raman spectroscopy performed at room temperature in the range 100–1000 cm^{-1}, as shown in Figure 2. The results of Raman spectroscopy and absorption spectra of the synthesized nanomaterial confirmed the formation of composite heterostructures. A typical Raman spectrum of the synthesized nanostructures reveals bands associated with the presence of copper and zinc oxide phases that are simultaneously present in the spectrum. Namely, the spectrum contains bands at 220 and 323 cm^{-1}, corresponding to the vibrational bands of the Cu_2O and CuO structures (Wang J et al. 2011). The other characteristic peaks of copper oxides that are typically observed at around 600-630 cm^{-1} most probably appear as shoulders to a broad band with a maximum at 561 cm^{-1}. The latter band is attributed to the LO phonon mode of ZnO wurtzite structure (Wang J et al. 2011, Pal U et al. 2006, Song Y et al. 2019). In addition, band at 431 cm^{-1} is observed (E_2^{high} mode) (Pal U et al. 2006, Song Y et al. 2019), that together with above-mentioned band at 561 cm^{-1}

proves the presence of ZnO in the nanocomposite. Thus, coexistence of the Raman modes of ZnO and CuO in the Raman spectra confirms the formation of a composite ZnO/CuO nanostructure.

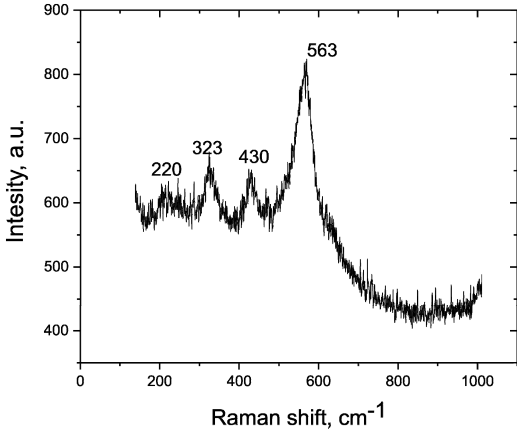

Figure 2. Raman spectrum of the ZnO/CuO composites deposited on the Cu substrate during the plasma activated electrolysis synthesis

To conclude, a novel approach based on simultaneous plasma-assisted anodic dissolution of constituent metals was proposed and tested towards the synthesis of composite CuO/ZnO NPs and thin films. The results demonstrate a simple versatile approach for composite multi-element oxides formation that can be expanded for the production of a broader range of nanomaterials.

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