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Abstract

Electrochemical Analysis of Rationally Designed ZnO Nanostructures for Biodegradable Cellular Scaffolds †

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Abstract: This work is a preliminary analysis of a wet-chemistry synthesized platform based on ZnO nanostructures (n-ZnO) for application in regenerative medicine. n-ZnO stability is investigated by electrochemical in situ sensing of zinc ions released by n-ZnO soaked in simulated biofluids. Impedance analysis allows detection of subtle changes in the bulk solution impedance up to 50 kHz, which can be ascribed to the release of ionic species in solution, among which are Zn^{2+} ions. In parallel, a voltammetry analysis using low-cost, mercury-free, screen-printed sensors shows the release of Zn^{2+} ions at concentrations that are not harmful.

Keywords: ZnO nanostructures; metal oxide crystals; impedance; zinc ion determination

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1. Introduction

The development of sustainable platforms for biodegradable cellular scaffolds requires the engineering of functional materials coupling versatile physicochemical properties, biocompatibility, and tunable stability in biofluids. A well-investigated material to this end is nanostructured ZnO [1]. ZnO nanostructure (n-ZnO) geometry influences both stability and functionality. For instance, ZnO nanoparticles are toxic toward different kinds of cell lines [2], due to a fast (<1 h) dissolution process. On the contrary, 1D n-ZnO is biocompatible, as reported by the Food and Drug Administration (21CFR182.8991) [3]. Nevertheless, the dissolution of n-ZnO occurs with kinetics of the order of some hours [4]. This can modify zinc homeostasis and lead to reactive oxygen species, which can trigger apoptosis [5]. In this scenario, there is still a lack in knowledge of n-ZnO stability when used as is or as filler within biocompatible matrixes. To fill this knowledge gap, this preliminary study leverages electrochemical detection methods based on electrical impedance and voltammetry to provide a first glance of the stability of n-ZnO in aqueous solutions.

2. Materials and Methods

n-ZnO growth is achieved in a 250 mL solution in ultrapure DI water with resistivity at 25 °C > 18.2 MΩ·cm (Direct-Q® 3 UV Water Purification Systems, Merck Millipore, Burlington, MA, USA). The solution contains 15 mM zinc nitrate hexahydrate (Sigma Aldrich, St. Louis, MO, USA, ≥99.0%), 7.5 mM hexamethylenetetramine (Sigma Aldrich, ≥99.0%), 0.10 M ammonia (Alfa Aesar, Haverhill, MA, USA, 28% v/v in water), 2 mM polyethylenimine (Sigma Aldrich, average Mw ≈ 800, average Mn ≈ 600), 5 mM potassium chloride (Fluka, Charlotte, NC, USA, >99.0%), and 15 mM monoethanolamine (Sigma Aldrich, ≥99.0%). The precipitates at the bottom of the container are collected, washed with DI water, dried at 60 °C for 24 h, and calcined at 200 °C for 2 h. Electrochemical measurements are carried out using Autolab PGSTAT128N (Metrohm AG, Herisau, Switzerland).

3. Discussion

The synthesized n-ZnO is analyzed by spectroscopic (UV-visible) and electrochemical (cyclovoltammetry) methods. Preliminary impedance measurements are conducted on n-ZnO (at 0.2 mg/mL concentration) dispersion in ultrapure water using two identical graphite electrodes soaked in the analysis solution. The solution impedance is measured from 5 min to 20 min and finally after 3 days. The resulting decrease in the electrical impedance is quantified by the reduction in the diameter observed in the Nyquist plot (Figure 1a), which shows the negative value of the imaginary versus the real parts of the complex impedance. Ongoing experiments aim at the voltammetric determination of zinc ions using Britton–Robinson buffer (pH 7.0) as the background electrolyte [6]. To this end, anodic stripping detection of zinc on a disposable screen-printed gold electrode shows the zinc ion release from the n-ZnO at ppm levels (Figure 1b). Whereas in principle, zinc ions in biofluids could pose a challenge for living cells, this preliminary study shows that the released zinc ions are at concentrations below the limits that would cause dyshomeostasis. Ongoing studies are looking at the preparation of n-ZnO–cellulose composites for minimizing such zinc ion leakage into solution.

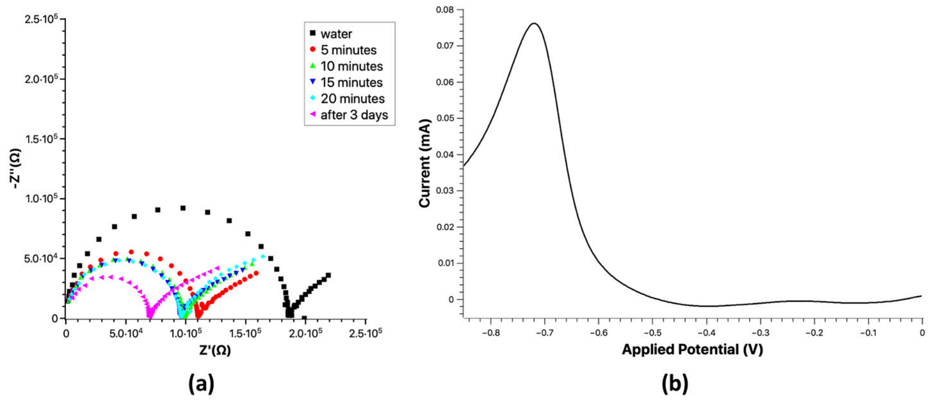

Figure 1. Direct sensing of n-ZnO effect in aqueous fluids. (**a**) Time-dependent analysis of the impedance of solution containing n-ZnO. (**b**) Preliminary voltammetric determination of zinc ions.

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