Three-Dimensional Printing of ZnO Macrostructures with Antibacterial Properties and Low Resistivity

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Principal Investigators: Christopher Kemper Ober[1], Tobias Hanrath[2]

User: Dung-Yi Wu[1]

Affiliations: 1. Materials Science and Engineering, 2. School of Chemical and Biomolecular Engineering; Cornell University

Primary Source of Research Funding: National Science Foundation

Contact: christopher.ober@cornell.edu, dw567@cornell.edu

Website: http://cober.mse.cornell.edu/index.html

Primary CNF Tools Used: Scanning electron microscope (SEM)

Abstract:

We report the first 3D-printable ZnO nanoparticles (NPs) for digital light processing that enable the fabrication of arbitrary and complex 3D metal oxide patterns at room temperature. By modifying photosensitive methacrylic acid on ZnO NPs (ZnO-MAA NPs), we demonstrate the continuous production of programmed 3D structures purely from the nanoscale building blocks. The printed image had good resolution and a height variation of only several nanometers. Printed ZnO-MAA NPs possessed better antibacterial properties than commercial PMMA. Also, calcined ZnO structures demonstrate lower resistivity and rectifying behavior.

Summary of Research:

Additive manufacturing, also known as three-dimensional (3D) fabrication, is a rapidly advancing technique that uses layer-by-layer deposition of materials to construct 3D objects [1]. Compared with traditional manufacturing techniques, 3D printing has significant advantages such as the availability of a wide selection of printing materials, the absence of a need for molds and the ability to create highly complex products [2].

In recent years, digital light processing (DLP) has proven to be one of the most promising 3D printing techniques due to its high resolution, faster printing speed and lower manufacturing cost [3]. DLP is analogous to photolithography as they both create structures using a photosensitive material to crosslink the matrix when exposed to ultraviolet (UV) light [4]. Extensive research has focused on printing polymer-based materials for applications such as micro-fluidic devices, biochips and scaffolds [5]. However, printing materials other than organic polymers, such as metal oxides, is still a challenge for the DLP method. Although some research has been devoted to overcoming this material limitations, the main ingredient in this process remains an organic polymer. Therefore, it is essential to develop a way to process inorganic ingredients to broaden the material choice for 3D printing.

Metal oxides possess many impressive properties, such as optical and environmental resistance. ZnO is one of the most commonly studied metal oxide. It is well-known for its wide and direct band gap, transparency, nontoxicity, good stability, antibacterial properties and biocompatibility [6], which enable applications in semiconducting devices, environmental remediation and as antimicrobial agents. Herein, we propose 3D-printable ZnO building blocks having photoresponsive ligands, specifically methacrylic acid (MAA), on the surface of NPs.

Figure 1 demonstrates a schematic diagram on how 3D structures were precisely constructed from the nano-to macro-scale based on the crosslinking of the building units. MAA ligands play a critical role in increasing colloidal stability, and act as a molecular connector that

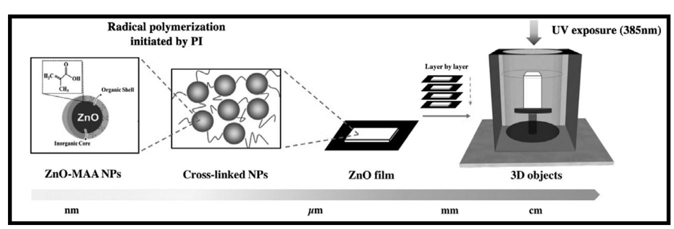

Figure 1: A schematic diagram illustrating the reactions of precursor ZnO-MAA NPs that crosslinked to form a ZnO film. The film was built up layer-by-layer to form three-dimensional (3D) objects.

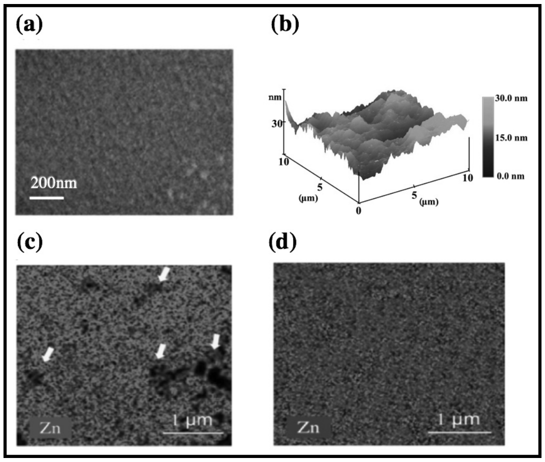

Figure 2: (a) Scanning electron microscopy (SEM) image of a layer of ZnO film. (b) AFM images of ZnO films showing 3D topographies (scale bar: 10 μm × 10 μm × 30 nm). (c) SEM-EDX spectroscopy analysis of a ZnO-MAA NPs film formed by photopolymerization.

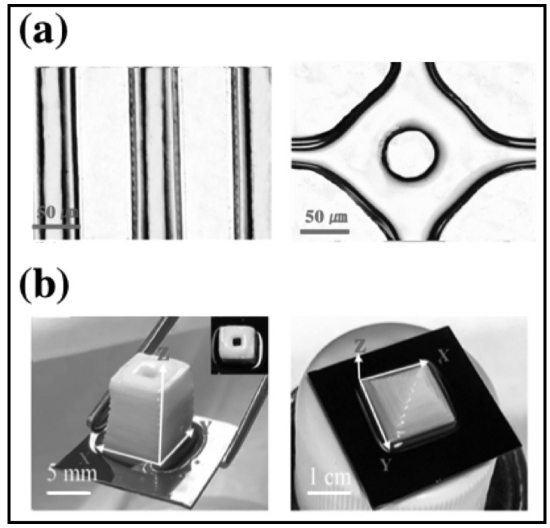

Figure 3: (a) Parallel lines, bent corners and a square array with voids. (b) Honeycomb, butterfly and Cornell logo microstructures printed by the digital light processing technique. (c) Hollow cuboid, pyramidal and townhouse 3D structures manufactured by this technique.

offers interconnection strength for building up the 3D structures. In Figure 2 (a), it is shown that the surface of the film made by ZnO NPs is smooth and uniform. Figure 2(b) shows 3D topographies of an amorphous ZnO film imaged in the tapping mode. The height variation was less than several nanometers. Compared to physical blending, SEM-EDS spectroscopy analysis of ZnO film building from ZnO NPs indicates ZnO particles are distributed more homogenously in Figure 2(c). The height variation was less than several nanometers.

We used optical microscopy and SEM images to judge the resolution limitation in Figure 3(a). They revealed that the printed sample had good resolution reaching 50 μm and Figure 3(b) shows printed ZnO 3D structures. Furthermore, the antibacterial activity was assessed using *E. coli* and *S. aureus* bacteria; a strong inhibition effect was observed with the 3D-printed ZnO sample in Figure 4 (a). After calcination, the resistivity of 3D-prinited ZnO dropped to 62 Ω·m and showed rectifying behavior in Figure 4(b). This study suggests the possibility, but not limited to, of using metal-oxide customized 3D printed structures to make antimicrobial products and semiconducting devices.

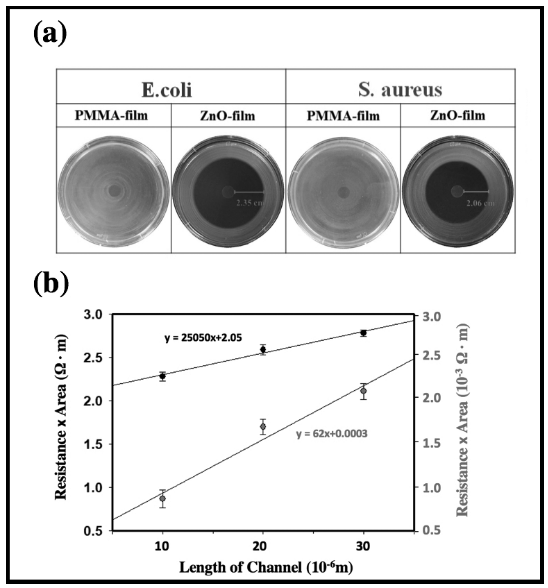

Figure 4: (a) Exposure course of the inhibition zones and (b) Cell counts for the growth of E. coli and S. aureus cells on PMMA and ZnO films. Resistivity of ZnO film (c) before (black dots) and after calcination (red dots) at 700°C.

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