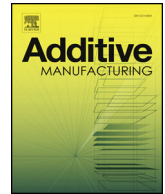




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Projection based light-directed electrophoretic deposition for additive manufacturing



Jeronimo Mora, Jessica K. Dudoff, Bryan D. Moran, Joshua R. DeOtte, Wyatt L. Du Frane, Joshua D. Kuntz, Andrew J. Pascall*

Lawrence Livermore National Laboratory, Livermore, CA, 94550, USA

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ABSTRACT

Electrophoretic deposition (EPD) is a widely used industrial coating technique for depositing polymer, ceramic, and metal thin films. Recently, there has been interest in using EPD for additive manufacturing using reconfigurable electrodes. Here, we report the first projector-based light-directed electrophoretic deposition (EPD) system that uses projected digital masks to dynamically control the electric field, eliminating the need for physical photomasks. We demonstrate a resolution limit of 10 μm for the deposited feature, which corresponds to the limits of the optical system. Furthermore, the first 3D overhanging structure made with EPD is presented, which points to the ability to create architected cellular materials. These improvements open the possibility for EPD to be a true 3D additive manufacturing technique.

1. Introduction

Electrophoretic deposition (EPD) is a process where charged particles in suspension are driven to electrodes by electric fields where they deposit. There is a growing interest in using EPD as a manufacturing method because of its compatibility with a vast material set including metals [1], ceramics [2,3], biomaterials [4,5], polymers [6,7], semiconductors [8], and composites [9,10], and its speed, with depositions typically lasting from seconds to minutes and can yield deposits several centimeters thick [11]. It has been successfully used in a wide variety of applications such as solid-state lighting [12,13], reactive materials [14], energy storage [15,16], drug delivery [17,18], and photovoltaics [19]. While EPD has seen adoption at the industrial scale [20], it has traditionally been viewed as a conformal film deposition technique for producing monolithic or, at most, graded or layered composites where the gradient is along the deposition direction [21]. Full control of deposited material gradients, both in-plane and along the deposition direction, requires electrodes that can be reconfigured during deposition.

A few researchers have explored using movable or reconfigurable electrodes during the EPD process to create complicated gradients or free-standing films that could not be made with standard EPD processing. Notably, Anné, et al. used a series of 4 counter-electrodes to produce a near net shape functionally graded femoral ball head [22]. Nold, et al. were the first to truly explore the reconfigurable electrode concept when they presented both a movable coaxial cable electrode

setup as well as an addressable electrode array to localize deposits on a surface to create an EPD computer aided manufacturing system [23]. Pascall, et al. demonstrated forming composites with gradients both in-plane and along the deposition direction using light directed EPD [24]. In a follow on paper, they also used a light addressable counter electrode to create a patterned deposit on an unpatterned aluminum electrode which points to the utility of light directed EPD in additive manufacturing [25]. However, production of arbitrary 3D structures with overhanging features via EPD has heretofore been impossible.

Of late, there has been great interest in architected or cellular materials that exhibit properties that were previously unattainable with bulk materials. Generally, these designs require complex patterning of material over length scales on the order of 10s of microns [26,27], containing controlled porosity [28,29], and may require multiple constituent materials to function [30]. Microscale additive manufacturing techniques, such as photopolymer-based lithography, excel at printing small features and void space with high resolution, and indeed, many of the examples of architected materials appearing in the literature have used such techniques. However, the multi-material capabilities of these processes are limited to using multiple polymer resins [31] or loading particles into the resin [32]. As we have discussed, EPD is well-suited for multi-material deposition and has been proven at industrial scale, but patterning of fine features and voids generally has not been possible.

Pascall et al. have previously demonstrated a new additive

* Corresponding author.

E-mail address: pascall1@llnl.gov (A.J. Pascall).

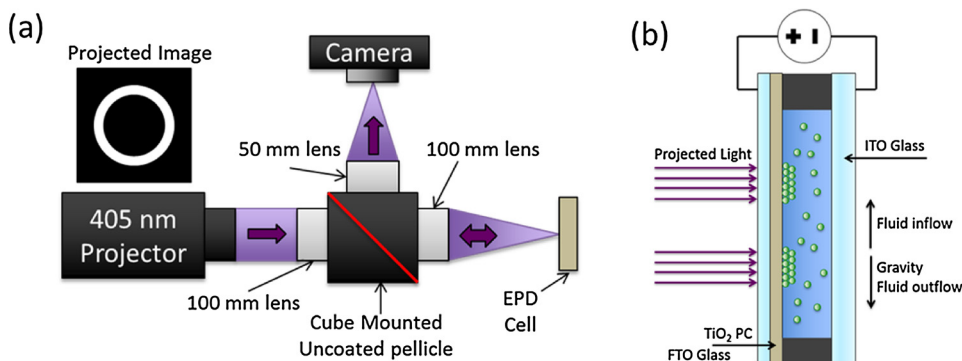


Fig. 1. (a) Illustration of the light-directed EPD light delivery system. (b) Detailed cross-sectional view of the EPD cell in (a). Projected light locally increases conductivity of the TiO_2 photoconductive layer which leads to a patterned electric field in the cell. Particles follow these field lines and deposit in regions of illumination.

manufacturing technique called “Light-Directed EPD” which involves the use of photoconductive electrodes, laser cut photomasks, and UV light to locally control the electric field [24,25]. The use of laser cut photomasks, while reconfigurable, limits the scalability, the ability to be automated, and the resolution of the technique to 100s of microns. This work expands on that of Pascall et al. by moving to a projection based system that not only removes the need to produce physical masks, but also allows the depositing pattern to change continuously throughout a run similar to projection stereolithography methods. This opens the door rapid fabrication of complex structures over large build areas. Furthermore, we explore the resolution limits of the technique and demonstrate that patterning of material at $10\ \mu\text{m}$ scale is possible. To our knowledge, we also present the first free standing bridge structure made with the EPD process.

2. Experimental setup

A schematic of light-directed EPD setup can be seen in Fig. 1. Deposition takes place inside a deposition cell consisting of a photoconductive substrate and a counter electrode separated by a spacer. The enclosed region is filled with a suspension of particles that will form the deposit. The photoconductive substrate is made of a hydrothermally grown layer of titania nanorods on a fluorine-doped tin oxide (FTO) coated fused silica substrate. The fabrication procedure for the photoconductive substrate is previously described in the literature [33,34] and is summarized in the supporting information. Patterning light is projected onto the back of the photoelectrode and a potential is applied between the counter electrode and the FTO layer. Illuminated regions become more conductive and electric field lines become localized to the regions of illumination. Particles are driven by the electric field to the surface where they deposit. By changing the projected light pattern and particle suspension, multi-material deposits can be formed in different regions corresponding to the light pattern [24].

Light patterning is performed with a computer controlled DMD projector with a monochrome 405 nm LED diode (CEL5500-LED, Digital Light innovations) and a series of lenses (Fig. 1a). The physical size of a projected pixel is $15\ \mu\text{m}$. A CMOS camera (DCC1545 M-GL, Thorlabs) with an attached absorptive neutral density filter of optical density 3.0 (NE30 A, Thorlabs) is placed at the focal point of the 50 mm achromat doublet to monitor the projected image on the deposition substrate in real time and assist in focusing the image. The projector was controlled using the Digital Light innovations CELconductor Control Software. Projected light intensity at the deposition plane was approximately $80\ \text{mW}/\text{cm}^2$ as measured by a power meter (PM100D with sensor S120VC, Thorlabs).

The complete deposition cell fabrication details were previously published [24] but are summarized here: The cell consists of two halves machined out of Delrin that when combined form a leak tight chamber. Each side has a 25 mm square, 1.1 mm deep recess to accept an electrode (either the photoelectrode or the counter electrode). A 22 mm

roughly square orifice is machined into each half to provide optical access to the back of the photoelectrode. The side that seats the counter electrode has a 25 mm wide, 250 μm deep recess for fluid flow and ports for suspension entry and exit. A 250 μm plastic spacer fixes the distance between the electrodes and ensures that they are parallel. Spring-loaded pin electrodes provide electrical contact through the cell to the back of the substrates.

2.1. Reconfigurable deposition

To demonstrate that rapid and dynamic patterning using light-directed EPD is possible, a three-step deposition was performed by consecutively depositing three different patterns for 30 s each (Fig. 2a). A 2 vol% suspension of tungsten nanopowder (US1158, US Research Nanomaterials, 70 nm particle size) was prepared in 100% ethanol with 0.24 vol% of Darvan 821 A as a surfactant. The suspension had a negative zeta potential. Details about the processing and zeta potential measurements are presented in the supporting information. With the empty deposition cell on a linear translation stage and the voltage off, a fully illuminated image was projected onto the photoelectrode. The cell was moved toward the projector until the back surface of the electrode came into focus on the camera. The cell was then moved forward approximately another millimeter until the top surface of the photoelectrode was in focus. The projected image was changed to a hollow square, and then the suspension was infused into the cell through the bottom fluid port. The infusion was stopped once fluid could be seen coming out of the top fluid port. The deposition occurred with the deposition electrode oriented parallel to gravity. ITO glass was used as the counter electrode. A +2 V DC bias was applied across the electrodes (the counter electrode was grounded) for 90 s (Fig. 1b) and a series of three images were projected onto the photoelectrode for 30 s each (Fig. S1 b–d). After the depositions were complete, the bias was lowered to 1 V DC and the suspension was withdrawn from the cell at 0.25 mL/min and the sample removed. Thus, complex parts can be formed rapidly and dynamically without the need for hard tooling, demonstrating the full automation of the light directed EPD technique.

2.2. Ultimate feature resolution

The ultimate feature resolution that can be created is one of the most important parameters for a given manufacturing technique. To determine the ultimate resolution, an EPD experiment was performed using the high resolution light delivery system of Zheng et al. [35] which demonstrated stereolithography features as small as $10\ \mu\text{m}$. This apparatus provides a higher projected spatial resolution than the setup described in Fig. 1, and was utilized solely to provide insight on the ultimate resolution of light directed EPD. Details about the construction of this optical system are provided in the supporting information. In this system, a single projected pixel has a physical dimension of $1.15\ \mu\text{m}$. The deposition cell was first filled with the tungsten suspension until

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