Recent Advances in Liquid-phase Electron-Beam Induced Deposition: Characterizing Growth Processes and Optical Properties

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Our group[1-4] and others[5] recently began studying focused electron-beam induced deposition (EBID) of deterministic nanostructures from bulk-liquids. This process, liquid-phase electron-beam induce deposition (LP-EBID), represents the convergence of EBID using gaseous precursors[6-8] and large area, quasi-random, electron-beam-based radiochemical synthesis of nanoparticles in liquids[9-11]. Likewise, this work is closely related to the observation of nanostructure growth in liquids using *in-situ* electron microscopy[12-13]. As illustrated in FIG. 1(a), we separate the liquid from the vacuum system by an electron-transparent membrane and typically deposit on the membrane itself. We have patterned several metals (Pt, Au, Ag, Ni, and Cr) with dimensions ranging from tens to hundreds of nanometers using aqueous solutions containing various precursor ions and ion complexes. Here we review our efforts to characterize Pt deposition on various substrates[1-3], gold deposition from two ionic complexes (chloroaurate and disulfitoaurate)[4], and silver, nickel, and chromium deposition from nitrate, chloride, and sulfate salts. Compared to gas-phase EBID, liquid precursors often enable deposition of higher purity materials at comparable resolution and with easily accessible precursors. In addition, we discuss new experiments that study the nucleation and growth of platinum nanoparticles and that study the localized surface-plasmon resonances of deposited silver nanoparticles.

Real-time electron microscopy during LP-EBID allows one to simultaneously induce and monitor the growth of nanostructures. Despite the complexity of using the electron-beam for both deposition and imaging, such experiments provide insight into the growth process. In this case, we separated the nucleation and growth steps by depositing Pt nanoparticles and subsequently allowing the particle to grow while imaging. Custom stainless steel liquid cells with a 150-nm thick Si_xN window were loaded with an aqueous solution of chloroplatinic acid (H_2PtCl_6, 1wt.%). Nucleation, growth, and imaging were carried out with a 20keV beam energy and 1.3 nA current in a Raith e_LiNE e-beam lithography system. Pt deposits were nucleated with a single pixel dose of 4 nC. A hemispherical particle, typical of high dose deposition on Si_xN, is shown in FIG 1(b). Subsequently, the deposit was imaged using a normal SEM raster scan during which time the particle grew. This allowed observation of particle growth for about 8 minutes until the imaging process nucleated other particles nearby. Frames from a typically growth sequence are shown in FIG. 1(c).

In separate experiments, Ag nanoparticles were deposited from solutions of silver nitrate ($AgNO_3$) on the polyimide membrane of commercial Quantomix liquid cells. As shown in FIG. 2(a,b), careful control of the precursor concentration yielded distinct nanoparticles with minimal "collateral" deposition. We previously characterized LP-EBID Ag deposits from $AgNO_3$ solutions using EDS and found slight sulfur contamination (~5at.%) and the possibility of Cl contamination. This level of purity encouraged us to study of the optical properties of the particles, and transmission measurements were carried out using a custom built microspectroscopy system. FIG. 2(c) shows the extinction spectrum of a 1-um pitch Ag particle array surrounded by water. The extinction peak near 420 nm is consistent with the transverse localized surface plasmon resonance of a Ag particle. Thus, LP-EBID may prove useful for rapidly prototyping nanophotonic devices.[14]
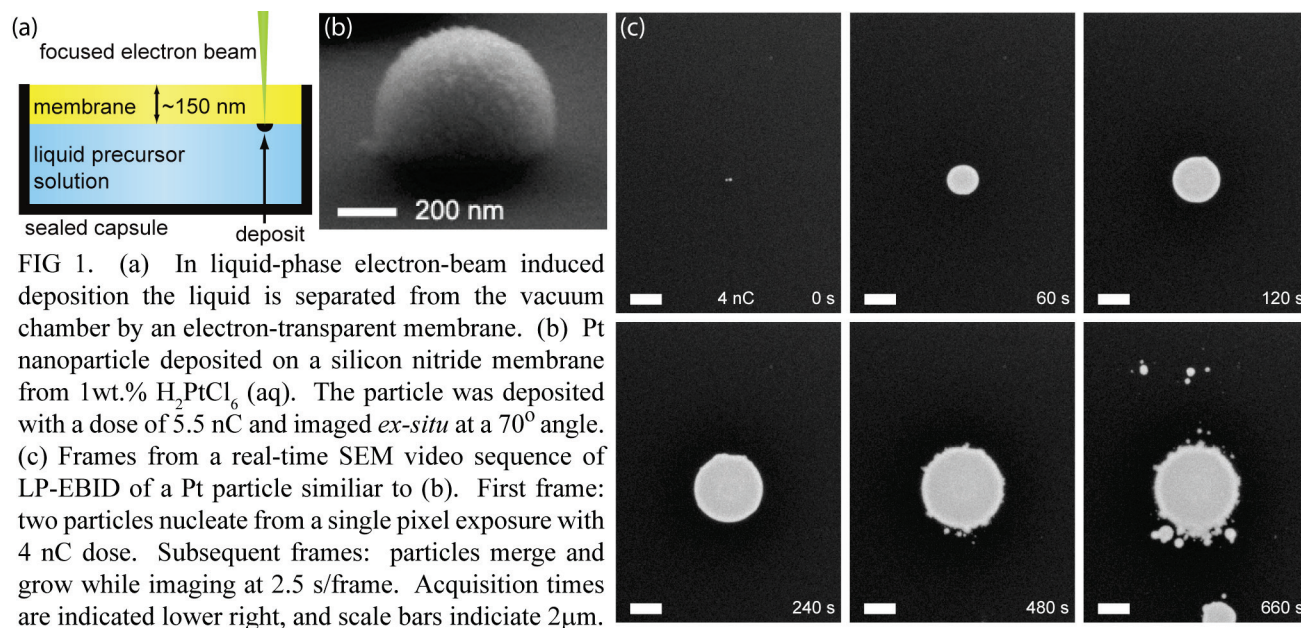
FIG 1. (a) In liquid-phase electron-beam induced deposition the liquid is separated from the vacuum chamber by an electron-transparent membrane. (b) Pt nanoparticle deposited on a silicon nitride membrane from 1wt.% H_2PtCl_6 (aq). The particle was deposited with a dose of 5.5 nC and imaged *ex-situ* at a 70° angle. (c) Frames from a real-time SEM video sequence of LP-EBID of a Pt particle similiar to (b). First frame: two particles nucleate from a single pixel exposure with 4 nC dose. Subsequent frames: particles merge and grow while imaging at 2.5 s/frame. Acquisition times are indicated lower right, and scale bars indiciate 2μm.
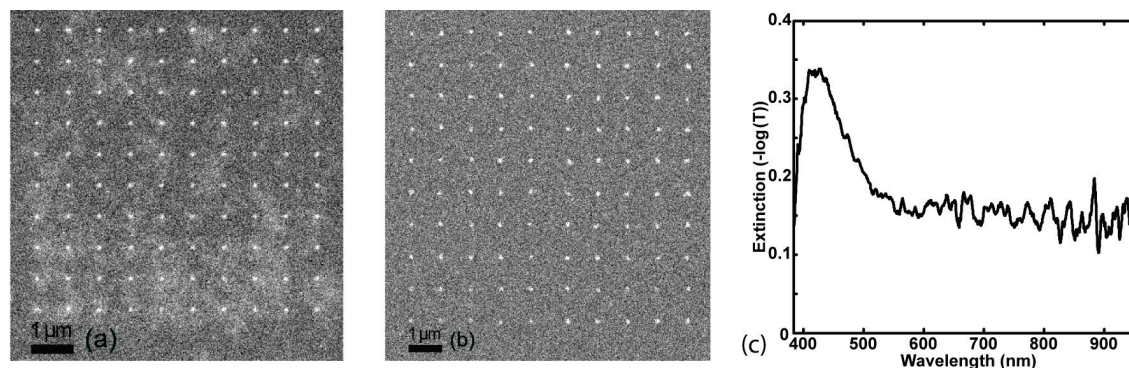

FIG 2. (a) 1-μm pitch array of silver nanoparticles (~100 nm diameter) deposited from 1.0 mM $AgNO_3$ (aq) with a dose of 75 pC/particle. Note "collateral" deposition between particles. (b) Identical array deposited from 0.75 mM $AgNO_3$ requires higher dose (250 pC/particle), but exhibits greatly reduced collateral deposition. Deposition from lower concentrations yielded incomplete patterns. Images were taken *in-situ,* and low signal-to-noise ratios were required to prevent additional deposition during imaging. (c) Optical extinction spectrum from the array in (b) showing a peak at 420 nm corresponding to a localized surface plasmon resonance of the nanoparticles.

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