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Polymer nanoliter well arrays for liquid storage and rapid on-demand electrochemical release

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ABSTRACT

Polymer microfluidic systems are of increasing importance in several applications in biomedicine and biosensing. The integrated encapsulation, storage, and controlled release of small amounts of liquid in such systems remains an unresolved technical challenge. Here, we report two methods for the room-temperature and adhesive-free sealing of 1–330 nanoliter volumes of liquid in off-stoichiometry thiol-ene polymer well arrays by spontaneous bonding to 200 nm thin gold films. Sealed well arrays were stored for more than one month in a liquid environment with <10% liquid loss, and for more than one week in air with minimal loss. We demonstrated that controlling the electrical potential and polarity over encapsulated wells allowed for selecting one of two well opening mechanisms: slow anodic electrochemical etching, or rapid electrolytic gas pressure-induced bursting of the gold film. The results may find potential applications in diagnostic testing, in vivo drug delivery, or in spatio-temporal release of chemical compounds in biological assays.

1. Introduction

Polymer microfluidic systems are increasingly used for a wide range of biomedical applications, e.g. in microanalytical systems, as well as in life science research, e.g. for organs-on-a-chip. The choice for polymer platforms for those applications is driven by their potential for biocompatible operation, the level of functional integration that can be achieved, the relative ease and cost-efficiency of device development and fabrication, and the optical transparency, allowing for the visual detection and monitoring of on-chip biological/biochemical processes.

Integrated storage and release of reagents in microfluidic platforms [1–4] enable hands-off operation and reduces the need for external interfacing. Despite previous progress [5–10], integrated encapsulation, storage and release of nanoliter to microliter volumes of aqueous solutions in polymer microfluidic devices face unresolved technical challenges. Specifically, tiny volumes of liquid are prone to evaporation during encapsulation and biological contents are prone to denaturation. In addition, encapsulation and release of biologically active substances must be performed under mild conditions, i.e. at low temperature and avoiding harsh chemicals or solvents.

We report the encapsulation, storage, and release of nanoliter to microliter volumes of aqueous liquid in polymer microwells. Our approach builds on the in-situ, room-temperature sealing of off-stoichiometry thiol-ene (OSTE) [11–15] polymer nanoliter wells with a gold film (Fig. 1). The gold film has appropriate barrier properties and is sufficiently thin to enable liquid release by pneumatic pressure or by electrochemical etching [16,17] (Fig. 2). OSTE is photostructured [13–15] on top of a gold electrode surface to define nanoliter well arrays (Fig. 1a), after which liquid is encapsulated using either of two different methods; a first method, here called *floatation sealing*, utilizes floatation to transfer a thin gold sealing film on top of a liquid filled well array (Fig. 1b); a second method, here called *supported gold film sealing*, utilizes a photostructured OSTE top-layer integrated with a thin gold sealing film to seal a liquid-filled well array bottom layer (Fig. 1c). In both methods, the gold layer spontaneously bonds to unreacted thiol groups present on the OSTE surface, ensuring appropriate sealing of the wells [18,19]. Storage of the well arrays for an extended period of time is performed under an appropriate liquid buffer to prevent liquid loss by pervaporation through the polymer. We further demonstrate two modes of liquid release, controlled by the electric potential between the bottom and the top gold layer in the wells. A low potential difference causes anodic electrochemical etching [16,17,20,21] of the top sealing gold film, which opens the well

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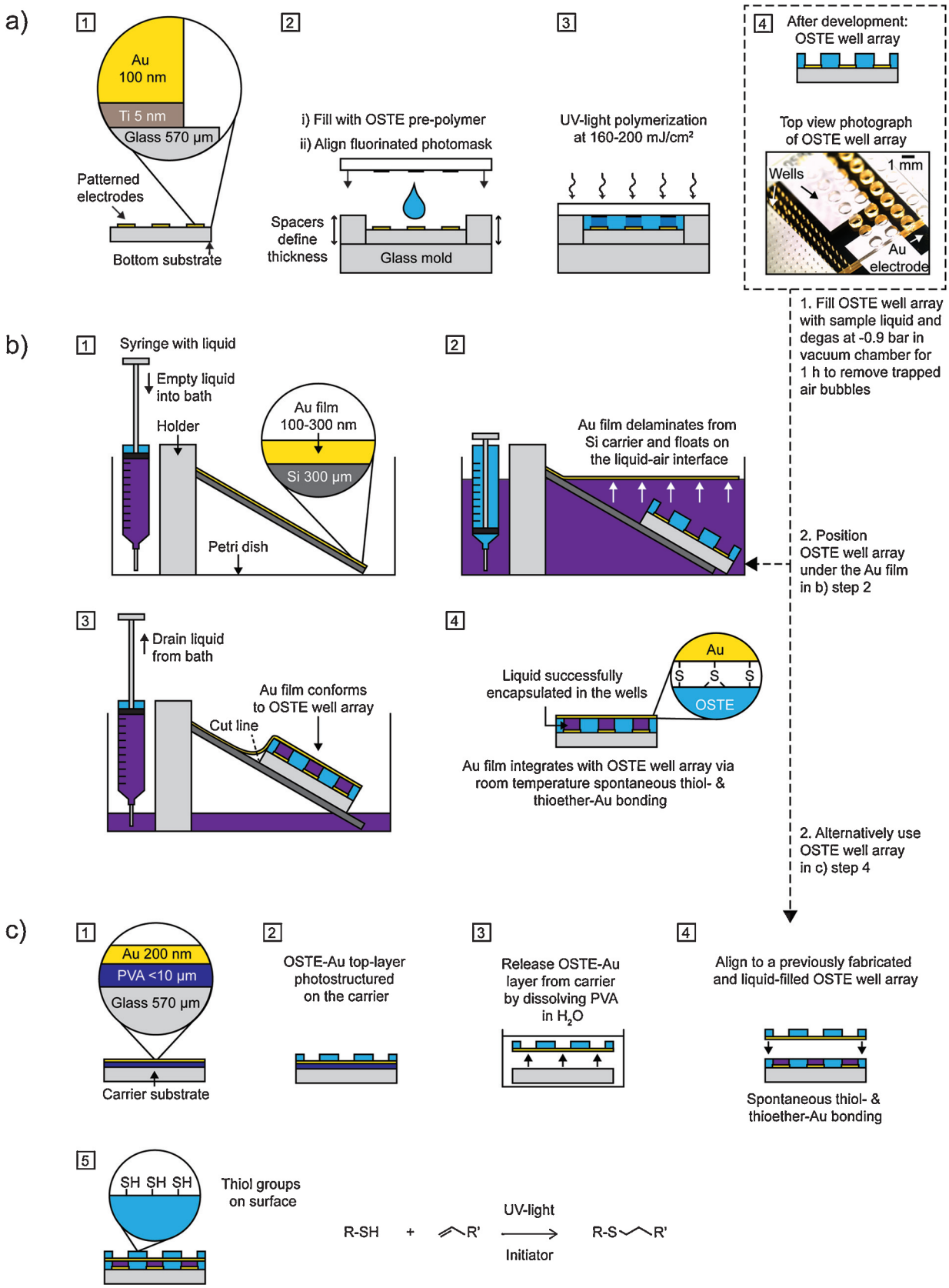

Fig. 1. Encapsulation of liquid in OSTE well arrays. a) Photostructuring of OSTE well arrays with gold electrodes on the bottom substrate: a1) cross-section of bottom substrate with patterned Ti/Au electrodes; a2) casting of liquid OSTE pre-polymer onto the bottom substrate; a3) photostructuring of OSTE via masked UV-light polymerization; a4) top: cross-section of well array after development; bottom: a top view picture of an OSTE well array on a gold electrode bottom substrate. The fabricated OSTE well array is subsequently sealed with b) floatation sealing, or c) supported gold film sealing, the latter enabling further microfluidic layer integration via thiol-ene click chemistry. b1) Cross-sectional view of the setup used in floatation sealing; b2) method to transfer the sealing gold film from a carrier substrate to the liquid-air interface of a bath with sample liquid; b3) the sealing gold film conforms and adheres to the liquid-filled